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UDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION

Part XXIX. The camphor-β-sulphonates (*d*-, *l*-, & *dl*-) of *o*-, *m*-, *p*-aminobenzoic acids, *p*-aminoazobenzene and *o*-toluoazo-*o*-toluidine

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Received July 30, 1947

The present investigation is in continuation of earlier work[1] and consists in the study of rotatory dispersion of camphor-β-sulphonates of *o*-, *m*- and *p*-aminobenzoic acids, *p*-aminoazobenzene and *o*-toluoazo-*o*-toluidine. One of the objects of the work is to study the effect of substituting the carboxyl group for hydrogen in *o*-, *m*- and *p*- positions in the benzene ring of the anilino camphor-β-sulphonates on the rotatory powers of the resulting compounds. Similarly the azo group has been included in this study. As these are all primary amine salts, the occurrence of mutarotation, where it occurs, has been ascribed to the change of the structure of the salt with the production of a ketimine or anil.

Influence of Wave Length on Rotatory Dispersion

The rotatory dispersion has been determined in the visible region of the spectrum for 12 wavelengths from λ 6708 Å.U. to λ 4358 Å.U. (Tables IV to VIII). It is found to be " simple " as it obeys the one-term Drude's equation, $[\alpha] = \frac{K_0}{\lambda^2 - \lambda_0^2}$. In this equation K_0, the " rotation constant," may be taken as the measure of ' absolute ' rotation for the wavelength λ for which $\lambda^2 - \lambda_0^2 = 1$ square micron. This value of λ is always in the infrared and is slightly greater than 10,000 Å.U. The ' absolute ' rotations (K_0) are thus numerically, but not dimensionally, identical with the magnitude of [α]. Comparison of rotatory powers and rotation constants at this wavelength, where $\lambda = \sqrt{1 + \lambda_0^2}$, may be regarded as those for corresponding conditions of wavelength, in which the effects of dispersion are eliminated.

The Physical Identity of Enantiomers

The rotatory powers of *d*- and *l*-enantiomers (Tables IV to VIII) are identical within the limits of experimental error and thus support Pasteur's

law of Molecular Dissymmetry, according to which the optical and their opposite isomers possess rotatory powers identical in magnitude but opposite in sign. Out of 302 observations, in as many as 293 cases the differences in the numerical value of the rotatory power of the dextro and lævo isomers correspond to a difference of 0·02° in the observed angle of rotation and in the remaining 9 cases this difference is 0·03° which is the limit of experimental error allowed in such measurements.

Nature of the Racemic Modification

The melting points of racemic modifications of camphor-β-sulphonates of *o*-aminobenzoic acid and of *o*-toluoazo-*o*-toluidine are higher than those of their optical isomers. They are, therefore, true *dl*-compounds. The melting point of the racemic form of camphor-β-sulphonate of *p*-amino benzoic acid is identical with those of its optical isomers whereas the melting points of the racemic forms of salts of camphor-β-sulphonic acid with *p*-amino azo benzene and *m*-aminobenzoic acid are lower than those of their optical isomers. That the racemic forms of these salts are also *dl*-compounds was determined in the following way: a small amount of the *d*-form was added to the corresponding racemic modification in each case and the melting point of the mixture was found to be lowered. This clearly shows that these racemic camphor-β-sulphonates are also true *dl*-compounds.

The Effect of Solvent on Rotatory Power

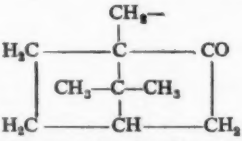
It is observed that the order of rotatory power of the position isomerides of salts of *o*-, *m*-, and *p*-aminobenzoic acids with camphor-β-sulphonic acids for Hg_{5461} in different solvents is pyridine > ethyl alcohol > methyl alcohol > water (Table I), whereas the sequence of increasing dielectric constant of the solvent is pyridine (12·4) < ethyl alcohol < (25·8) < methyl alcohol (31·2) < water (80). Hence it is obvious that the sequence of dielectric constants of the solvents follows the same order as that of rotatory power but in the opposite sense.

In the case of salts of camphor-β-sulphonates with *p*-aminoazobenzene it is, however, found that the order of decreasing rotatory power for Li_{6708} is methyl alcohol > pyridine which is also the sequence of their dielectric constants.

As already pointed out in our previous work it would, however, be more rational to compare the rotatory power of the solutions with their dielectric constants and not with the dielectric constants of the solvents.

TABLE I

No.	Structural formula	Solvent				
		Water (80)†	Methyl Alcohol (31·2)	Ethyl Alcohol (25·8)	Pyridine (12·4)	Chloroform (5·2)
1	*R·SO_3H·NH_2	‡20·50 ‖(3·400)	32·40 (6·284)	36·40 (6·997)	36·10 (7·57)	45·30 (9·276)
2	R·SO_3H·H_2N (COOH)	20·50 (3·56)	30·50 (5·95)	32·50 (6·271)	36·0 (7·123)	..
3	R·SO_3H·H_2N (COOH)	19·50 (3·335)	29·00 (5·697)	30·00 (5·618)	34·50 (6·935)	..
4	R·SO_3H·H_2N (COOH)	20·00 (3·475)	27·00 (5·113)	31·00 (5·777)	35·50 (7·139)	..
5	R·SO_3H·H_2N (N=N)	..	24·00§	..	15·00§ (4·01)	..
6	R·SO_3H·H_2N (CH_3, N=N, CH_3)	..	..	..	21·00§ (7·535)	..

* R = $C_{10}H_{15}O$ or 

† The figures in brackets stand for the dielectric constant of the solvent.

‡ Rotations are for Hg_{5461}.

§ Rotations are for Li_{6708}.

‖ The values for rotation constant, K_0 (absolute rotation) are given in brackets.

¶ These values are taken from Singh, B. K., *et al.*, *Proc. Lahore Phil. Soc.*, 1944, **6**, 15.

THE MOLECULAR ROTATORY DISPERSION OF CAMPHOR-β-SULPHONATES IN AQUEOUS SOLUTION AND COMPARISON OF THE VALUE OF $(M)_D^{35°}$ OF CAMPHOR-β-SULPHONATE ION IN WATER

Table II gives the values of $[M]_\lambda^{35°}$ in aqueous solution for salts of *o*-, *m*- and *p*-aminobenzoic acids with camphor-β-sulphonic acids. The mean value of $[M]_D^{35°}$ for the camphor-β-sulphonic ion is 53-54°. The value of $[M]_D^{35°}$ for the salts of *o*-, *m*- and *p*-aminobenzoic acids with camphor-β-sulphonic acid is 56·63°, 55·98° and 57·52° respectively. As these values of the rotatory power of the salts are slightly higher than the mean value

TABLE—II

No	Camphor-β-sulphonates of	Concentrates in gm./100 ccs.	$[M]_{\lambda}^{35°}$ in aqueous solution												
			Li 6708	Cd 6438	Li 6104	Na 5893	Hg 5780	Hg 5461	Ag 5209	Cd 5086	Cd 4800	Cd 4678	Li 4603	Hg 4358
1	1-carboxy-2-aminobenzene	1·0000	40·36	45·28	52·94	56·63	62·69	75·65	89·54	97·95	124·2	139·4	150·7	200·8
2	1-carboxy-3 aminobenzene	1·0000	38·19	42·91	50·21	55·98	59·51	71·91	85·23	93·35	118·7	133·6	144·4	193·6
3	1-carboxy-4-aminobenzene	1·0000	39·41	44·20	51·69	57·52	61·17	73·79	87·34	95·52	121·2	135·9	146·9	184·7

TABLE III

No.	Camphor-β-sulphonate of	$[\alpha]_{5461}^{35°}$			
		Water	Methyl Alcohol	Ethyl Alcohol	Pyridine
1	Aniline‡ ..	*20·50 †(3·400)	32·40 (6·284)	36·40 (6·997)	36·10 (7·57)
2	*o*-toluidine‡ ..	19·87 (3·367)	29·60 (5·685)	34·74 (6·88)	36·20 (7·93)
3	*o*-nitraniline§ ..	..	29·97 (3·973)	29·50 (3·666)	31·96 (4·051)
4	*o*-amino benzoic acid ..	20·50 (3·56)	30·50 (5·95)	32·50 (6·27!)	36·00 (7·123)
5	*o*-chloraniline‖ ..	18·97 (3·078)	26·96 (4·251)	28·97 (5·058)	32·50 (5·379)
6	*m*-toluidine‡ ..	18·80 (3·31)	28·90 (5·661)	34·10 (6·79)	35·50 (7·74)
7	*m*-nitraniline§ ..	..	34·47 (5·882)	35·38 (5·432)	35·97 (5·185)
8	*m*-aminobenzoic acid ..	19·50 (3·555)	29·00 (5·697)	30·00 (5·618)	34·50 (6·953)
9	*m*-chloraniline‖ ..	20·00 (3·644)	32·00 (6·386)	34·00 (6·945)	34·46 (6·541)
10	*p*-toluidine‡ ..	20·20 (3·39)	30·47 (5·96)	35·50 (6·95)	37·60 (7·81)
11	*p*-nitraniline§ ..	..	30·47 (4·536)	30·42 (4·195)	31·42 (4·782)
12	*p*-aminobenzoic acid ..	20·00 (3·475)	27·00 (5·113)	31·00 (5·777)	35·50 (7·139)
13	*p*-chloraniline‖ ..	18·98 3·510	31·50 (6·276)	33·50 (6·689)	36·00 (6·42)

* The values refer to $[\alpha]_{5461}^{35°}$

† The values for rotation constant K_0 (absolute rotation) are given in brackets.

‡ The values are taken from Singh, B. K., *et al.*, *Proc. Lahore Phil. Soc.*, 1944, **6**, 15.

§ The values are taken from Singh, B. K., and Perti, O. N., *Proc. Ind. Acad. Sci.*, A, 1945, **22**, 84.

‖ The values are taken from Singh, B. K., and Perti, O. N., *ibid.*, 1945, **22**, 265.

of $[M]_D^{35°}$ of the camphor-β-sulphonate ion (53·54°) and as the observed molecular rotatory power of the salt in aqueous solution is the sum of the rotatory powers of the active acid ion and the non-ionised molecule, it is clear that the undissociated molecule has higher rotatory power and that these salts are not completely electrolytically dissociated in 1 per cent. aqueous solution.

The Effect of Substituent Groups on Rotatory Power

Substituent groups arrange themselves in the following polar series deduced from measurements of inductive capacities:

OH^-, Cl, Br, I, CH_3, H^+, COOH, CHO, $COCH_3$, CN, NO_2^+

In Table (III) the values of $[\alpha]^{35°}_{5461}$ in different solvents are given. The values of K_0, the rotation constants, as above defined, are also given in brackets for the sake of comparison.

Ortho substitution.—On comparing the values of $[\alpha]^{35°}_{5461}$ in water, it is found that $-CH_3$, $-COOH$ AND $-Cl$ groups cause a decrease in the

Table IV. 1-*Carboxy*-2-*aminobenzene-camphor-β-sulphonates*

Solvent	Water		Methyl alcohol		Ethyl alcohol		Pyridine	
Concentration in gms./100 c.c.	*d*- 1·0000	*l*- 1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
Calculated $[\alpha]$	$\pm \frac{3·56}{\lambda^2 - ·1246} + 0·3529$		$\pm \frac{5·95}{\lambda^2 - 0·1064} + 0·3262$		$\pm \frac{6·271}{\lambda^2 - 0·1053} + 0·3245$		$\pm \frac{7·123}{\lambda^2 - ·1005} + 0·3170$	
Calculated λ_0								
Line	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	-d-	*-l-*	*-d-*	*-l-*	*-d-*	*-l-*	*-d-*	*-l-*
Hg_{4358} ..	+54·00	−55·00	+70·50	−69·00	+74·00	−75·50	+79·50	−80·50
Li_{4603} ..	41·50	40·50	56·50	55·00	58·00	58·50	64·00	65·00
Cd_{4678} ..	39·00	38·50	53·00	52·00	54·00	55·00	59·50	60·00
Cd_{4800} ..	34·00	33·00	47·00	48·00	50·50	50·00	53·50	54·00
Cd_{5086} ..	26·50	26·50	38·00	38·50	41·00	41·00	45·50	45·00
Ag_{5209} ..	24·00	24·50	35·50	35·50	37·50	38·00	40·50	40·50
Hg_{5461} ..	20·50	20·50	30·50	30·50	32·50	32·50	36·00	36·00
Hg_{5780} ..	16·50	17·00	25·50	26·00	27·50	27·50	30·00	30·50
Na_{5893} ..	15·50	15·50	24·00	24·50	26·00	25·50	28·00	28·50
Li_{6104} ..	14·00	14·00	21·50	22·00	23·50	23·50	25·00	26·00
Cd_{6438} ..	12·50	13·50	18·50	19·00	20·50	20·00	23·50	23·00
Li_{6708} ..	11·00	11·50	17·00	16·50	18·00	18·00	20·50	20·00
	No mutarotation		No mutarotation		Value for Hg_{5461} after 24 hours $[\alpha]^{35°}_{5461} = +28·50°$, for *d*-salt $[\alpha]^{35°}_{5461} = +29·00°$, for *l*-salt		No mutarotation	

TABLE V. 1-*Carboxy*-3-*aminobenzene-camphor*-β-*sulphonates*

Solvent	Water		Methyl alcohol		Ethyl alcohol		Pyridine	
Concentration in gms./100 c.c.	*d*- 1·0000		1·0000		1·0000		1·0000	
	l- 1·0000		1·0000		1·0000		1·0000	
Calculated $[\alpha]_{\lambda_0}$	$\pm \frac{3\cdot355}{\lambda^2 - \cdot1261}$ 0·3551		$\pm \frac{5\cdot697}{\lambda^2 - \cdot1017}$ 0·3189		$\pm \frac{5\cdot618}{\lambda^2 - \cdot1109}$ 0·3330		$\pm \frac{6\cdot953}{\lambda^2 - \cdot0967}$ 0·3110	
Line	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Hg_{4358} ..	+52·50°	−53·50°	+64·50°	−63·00°	+71·00°	−71·00°	+74·50°	−73·50°
Li_{4603} ..	..	..	52·00	51·50	55·00	55·50	61·50	60·00
Cd_{4678} ..	36·50	36·00	49·00	48·50	53·50	52·00	57·00	56·00
Cd_{4800} ..	31·50	33·00	44·50	44·00	47·50	48·00	52·50	53·00
Cd_{5086} ..	26·00	25·00	36·00	36·50	38·00	38·00	44·00	42·50
Ag_{5209} ..	23·00	23·00	33·50	34·00	35·50	35·00	39·50	40·00
Hg_{5461} ..	19·50	19·50	29·00	29·00	30·00	30·50	34·50	34·50
Hg_{5780} ..	15·50	16·00	24·00	24·00	25·50	25·00	29·00	29·50
Na_{5893} ..	14·50	14·50	23·50	23·00	23·50	24·00	27·50	27·50
Li_{6104} ..	13·50	13·50	21·00	21·50	21·50	21·50	24·50	25·50
Cd_{6438} ..	11·50	12·00	18·00	19·00	18·00	19·00	21·50	21·00
Li_{6708} ..	10·50	10·00	16·50	16·00	17·00	16·50	19·50	20·00
	No mutarotation		No mutarotation		Value for Hg_{5461} after 24 hours $[\alpha]^{35°}_{5461} = +22·50°$, for *d*-salt $[\alpha]^{35°}_{5461} = +22·00°$, for *l*-salt		No mutarotation	

rotatory power in the order H = COOH > CH_3 > Cl, whereas the order of decreasing values of K_0 is COOH > H > CH_3 > Cl. Thus the groups CH_3 and Cl behave in the opposite sense from COOH, in conformity with the above mentioned polar series. This however, does not hold good in other solvents.

In methyl alcohol and ethyl alcohol it is found that the substituent groups CH_3, Cl, COOH and NO_2 cause a decrease in the values of both $[\alpha]^{35°}_{5461}$ and K_0. The order for $[\alpha]^{35°}_{5461}$ in methyl alcohol being H > COOH > NO_2 > CH_3 > Cl and for K_0, H > COOH > CH_3 > Cl > NO_2. The order for $[\alpha]^{35°}_{5461}$ in ethyl alcohol is H > CH_3 > COOH > NO_2 > Cl and for K_0, H > CH_3 > COOH > Cl > NO_2. In neither case it agrees with the above mentioned polar series of the substituent groups.

On comparing the values of $[\alpha]^{35°}_{5461}$ in pyridine, however, it is found that the order of decreasing rotatory power is CH_3 > H > COOH > Cl

TABLE VI. 1-*Carboxy*-4-*aminobenzene-camphor*-β-*sulphonates*

Solvent		Water		Methyl alcohol		Ethyl alcohol		Pyridine	
Concentration in gm./100 c.c.	*d*-	1·0000		1·0000		1·0000		1·0000	
	l-	1·0000		1·0000		1·0000		1·0000	
Calculated $[\alpha]_{\lambda_0}$		$\pm \frac{3\cdot475}{\lambda^2-0\cdot1245}$		$\pm \frac{5\cdot113}{\lambda^2-\cdot1088}$		$\pm \frac{5\cdot777}{\lambda^2-\cdot1119}$		$\pm \frac{7\cdot139}{\lambda^2-\cdot1024}$	
		0·3528		0·3298		0·3348		0·3200	
Line		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
		d-	*l*-	*d*-	*l*-	*d*-	*l*	*d*-	*l*-
Hg_{4358}	..	+53·00°	−53·00°	+63·00°	−62·00°	+74·00°	+73·00°	+81·50°	−82·50°
Li_{4603}	..	40·00	39·00	49·00	49·50	58·00	57·00	65·00	65·50
Cd_{4678}	..	37·00	36·50	46·50	46·00	55·00	54·00	61·50	61·00
Cd_{4800}	..	32·00	33·00	42·00	42·00	48·00	49·00	55·50	55·00
Cd_{5086}	..	26·00	26·00	34·00	34·00	39·00	39·00	45·50	46·00
Ag_{5209}	..	23·50	23·50	32·00	31·50	36·00	36·00	42·00	42·50
Hg_{5461}	.	20·00	20·00	27·00	27·00	31·00	31·00	35·50	35·50
Hg_{5780}	..	16·50	16·00	22·50	23·00	26·00	25·00	31·00	30·50
Na_{5893}	..	15·50	15·50	21·50	21·50	24·00	24·00	28·50	29·00
Li_{6104}	..	14·00	14·50	19·50	20·00	22·00	22·00	26·00	26·50
Cd_{6438}	..	12·00	12·00	17·00	17·50	20·00	19·00	23·00	22·00
Li_{6708}	..	11·00	11·50	14·50	15·00	17·00	16·00	20·50	20·50
		No mutarotation		No mutarotation		Value for Hg_{5461} after 24 hours $[\alpha]^{35°}_{5461} = +3\cdot50°$, for *d*-salt $[\alpha]^{35°}_{5461} = -3\cdot50°$, for *l*-salt		No mutarotation	

$> NO_2$ which is also for K_0. This follows the order of polarity of the groups except in the case of Cl.

Meta substitution.—On comparing the values of $[\alpha]^{35°}_{5461}$ in water, the order of decreasing rotatory power is $H > Cl > COOH > CH_3$; in methyl alcohol $NO_2 > H > Cl > COOH > CH_3$, in ethyl alcohol $H > NO_2 > CH_3 > Cl > COOH$ and in pyridine $H > NO_2 > CH_3 > COOH > Cl$. In none of these cases the order agrees with that of polar series. On comparing the values of K_0 it is, however, found that in water the order is $Cl > COOH > H > CH_3$ and in pyridine, $CH_3 > H > COOH > Cl > NO_2$. This is in conformity with the polar series except for Cl. In methyl alcohol and ethyl alcohol the order is $Cl > H > COOH > NO_2 > CH_3$ and $H > Cl > CH_3 > COOH > NO_2$ respectively which does not agree with the above mentioned polar series.

Para substitution.—In the case of para substitution the order of $[\alpha]^{35°}_{5461}$ in water is $H > CH_3 > COOH > Cl$, in methyl alcohol, $H > Cl > CH_3$

TABLE VII. p-*Amino-azobenzene-camphor-β-sulphonates*

Solvent		Methyl alcohol		Pyridine	
Concentration in gm./100 c.c.	*d-*	1·0000		1·0000	
	l-	1·0000		1·0000	
Calculated	$[\alpha]$	..		$\pm \frac{4\cdot01}{\lambda^2-0\cdot1827}$	
	λ_0	..		0·4274	
Line		Obs. $[\alpha]$		Obs. $[\alpha]$	
		d-	*l-*	*d-*	*l-*
Li_{6708}	..	+24·00°	−25·50°	+15·00°	−15·50°
Li_{6104}	..	..	..	22·00	21·50
Na_{5893}	..	..	..	24·50	24·00
Na_{5780}	..	..	..	26·00	26·50
		Li_{6708} could not be read after 24 hours		No mutarotation	

TABLE VIII. o-*Toluoazo-o-toluidino camphor-β-sulphonates*

Solvent		Pyridine	
Concentration in gms./100 c.c.	*d-*	1·0000	
	l-	1·0000	
Calculated	$[\alpha]$	$\pm \frac{7\cdot535}{\lambda^2-0\cdot0732}$	
	λ_0	0·2706	
Line		Obs[α]	
		d-	*l-*
Li_{6708}	..	+21·00°	−20·50°
Li_{6104}	..	24·50	24·50
Na_{5893}	..	27·00	27·50
		Lines could not be read distinctly after 24 hours	

$= NO_2 > COOH$, in ethyl alcohol $H > CH_3 > Cl > COOH > NO_2$ and in pyridine $CH_3 > H > Cl > COOH > NO_2$. In the case of water and alcohols the sequence does not correspond to the polar series but in pyridine it is followed except for Cl.

The comparison of the values of K_0 shows that the order in water is $Cl > COOH > H > CH_3$ and in pyridine $CH_3 > H > COOH > Cl > NO_2$.

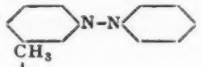
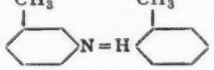
This is in conformity with polar series except for Cl. The order in methyl alcohol and ethyl alcohol is $H > Cl > CH_3 > COOH > NO_2$ and $H > CH_3 > Cl > COOH > NO_2$ respectively and does not agree with the polar series.

It is, therefore, clear that a better agreement is found with the above mentioned polar series of substituent groups for the values of K_0, the absolute rotation constant, and not for the values of $[\alpha]^{35°}_{5461}$, the specific rotatory power for an arbitrary wavelength. The groups COOH and NO_2 lying on one side of the hydrogen atom in the series behave similarly and opposite to the CH_3 group which falls on the other side.

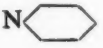
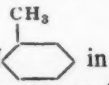
It is also evident that greater accord in rotatory power with the polar effect is found in the case of ortho substituents as might be expected from the closer proximity of the groups to the asymmetric centre in the molecule and is in conformity with our previous observations.[2]

The Effect of Azo Aryl Group on Rotatory Power

Table A

Structural formula	$[\alpha]^{35°}_{6708}$ in Pyridine
$R \cdot SO_3H \cdot H_2N$	21·20 (7·57)*
$R \cdot SO_3H \cdot H_2N$ 	15·00 (4·01)
$R \cdot SO_3H \cdot H_2N$	21·45 (7·93)
$R \cdot SO_3H \cdot H_2N$ 	21·00 (7·535)

* The values in brackets stand for K_0.

The effect of the substitution of H by $-N=N$  in anilino-camphor-β-sulphonates and by $-N=N$  in *o*-toluidino camphor-β-sulphonates is found to depress the rotatory power, though only very slightly in the latter case. A comparison of the values of K_0 also bears out the same result.

THE EFFECT OF POSITION ISOMERISM ON ROTATORY POWER

TABLE B

Solvent	$[\alpha]^{35°}_{5461}$
Water ..	$\begin{cases} m < p < o = Un \\ [m < Un < p < o] \end{cases}$
Methyl Alcohol ..	$\begin{cases} p < m < o < Un \\ [p < m < o < Un] \end{cases}$
Ethyl Alcohol ..	$\begin{cases} m < p < o < Un \\ [m < p < o < Un] \end{cases}$
Pyridine ..	$\begin{cases} m < p < o < Un \\ [m < o < p < Un] \end{cases}$

In Table (B) the order of rotatory power of position isomerides in different solvents for $[\alpha]^{35°}_{5461}$ is given, the order of K_0 is also given in square brackets. On comparing the values of $[\alpha]^{35°}_{5461}$, the sequence of position isomerides in all solvents is m < p < o < Un with the exception that in methyl alcohol the order is p < m < o < Un. Similar results with minor differences follow when a comparison is made for the values of K_0: the order of position isomerides in water is m < Un < p < o, in methyl alcohol p < m < o < Un, in ethyl alcohol m < p < o < Un, and in pyridine m < o < p < Un. These results, except in the case of methyl alcohol, do not agree with either Frankland's "lever arm" hypothesis[3] or with its electrostatic modification as suggested by Rule,[4] according to both of which the meta isomer should be intermediate between the ortho and para as regards its rotatory effect.

EXPERIMENTAL

The lævo and racemic forms of camphor-β-sulphonic acid were prepared in the same way as Reychler's acid[5] (*d*-camphor-β-sulphonic acid):

d-acid: found M.P. 197–8° C.; Eq. wt. = 231·6

l-acid: found M.P. 197–8° C.; Eq. wt. = 233·0

dl-acid: found M.P. 202–3° C.; Eq. wt. = 230·0

$C_{10}H_{15}O \cdot SO_3H$ requires Eq. wt. = 230·0

p-*Amino azobenzene camphor-β-sulphonates*

Molar proportions of *p*-aminoazobenzene and camphor-β-sulphonic acids were dissolved separately in hot ethyl acetate. The two solutions were then mixed and allowed to stand for sometime, when the salts crystallised out. They were repeatedly crystallised as long deep orange needles from

absolute alcohol and on drying in vacuum turned brick red. They are sparingly soluble in methyl alcohol and pyridine, less so in water and absolute alcohol and practically insoluble in acetone, chloroform and benzene.

Found: *d*-salt; M.P. 203°d-; S = 7·35%
l-salt; M.P. 203°d-; S = 7·32%
dl-salt; M.P. 200°d-; S = 7·63%
$C_{22}H_{27}N_3O_4S$ requires S = 7·45%

o-*Toluoazo*-o-*toluidino camphor-β-sulphonates*

Molecular proportion of *o*-toluoazo-*o*-toluidine and camphor-β-sulphonic acids were dissolved separately in hot ethyl alcohol. The two solutions were then mixed and allowed to stand when the salts crystallised out. They were repeatedly crystallised as long orange coloured needles and finally dried under vacuum when a yellowish brown powder was obtained. They dissolve in organic solvents giving deep orange red solutions. They are fairly soluble in pyridine and methyl alcohol, less so in chloroform and ethyl alcohol and practically insoluble in water and benzene.

Found: *d*-salt, M.P. 257–8°d-; S = 7·1%
l-salt, M.P. 257–8°d-; S = 7·25%
dl-salt, M.P. 262–4°d-: S = 7·18%
$C_{24}H_{31}O_4N_3S$ requires S = 7%

l-*Carboxy*-2-*aminobenzene- and* l-*carboxy*-3-*aminobenzene camphor-β-sulphonates*:

Molecular proportions of each of the amines and the camphor-β-sulphonic acids were dissolved separately in hot ethyl acetate. The two solutions were then mixed and allowed to stand when the salts crystallised out. They were then repeatedly crystallised as white needles from a mixture of ethyl alcohol and ethyl acetate and finally dried in vacuum. They are fairly soluble in water, ethyl alcohol, methyl alcohol and pyridine and practically insoluble in acetone, chloroform and benzene.

l-Carboxy-4-*aminobenzene camphor-β-sulphonates*

Molecular proportions of the amine and the acids were separately dissolved in ethyl alcohol and on mixing the two solutions, the salts crystallised out. They were repeatedly recrystallised from absolute ethyl alcohol as fine white needles. They are soluble in water, methyl alcohol and pyridine, sparingly so in ethyl alcohol but practically insoluble in acetone, chloroform and benzene.

Found: *o*-compounds:

d-salt, M.P. 154–6° C.; Eq. wt. 184·5; S = 8·35%

l-salt, M.P. 154–6° C.; Eq. wt. 184·5; S = 8·52%

dl-salt, M.P. 163–6° C.; Eq. wt. 183·3; S = 8·80%

m-compounds:

d-salt, M.P. 205° C.; Eq. wt. 184·5; S = 8·53%

l-salt, M.P. 205° C.; Eq. wt. 184·5; S = 8·90%

dl-salt, M.P. 200° C.; Eq. wt. 184·5; S = 8·90%

p-compounds:

d-salt, M.P. 284° d; Eq. wt. 184·5; S = 8·93%

l-salt M.P. 284° d; Eq. wt. 185·7; S = 8·62%

dl-salt, M.P. 284° d; Eq. wt. 183·3; S = 8·54%

$C_{17}H_{23}NO_6S$ requires Eq. wt. 184·5; S = 8·67%

The rotatory power determinations were made in a 2-dcm. jacketed tube at 35° C. The value of λ_0 calculated from the dispersion formula is given in Tables (IV to VIII) and is expressed as μ or 10^{-4} cm.

Summary

1. The rotatory dispersion of stereoisomeric salts of *o*-, *m*-, *p*- amino benzoic acids, *p*-aminoazobenzene and *o*-toluoazo-*o*-toluidine with camphor β-sulphonic acids is found, in different solvents, to obey Drude's one-term equation, $[\alpha] = \frac{K_0}{\lambda^2 - \lambda_0^2}$; it is, therefore, simple.

2. The *d*- and *l*-forms of these compounds possess identical rotatory power and thus further support Pasteur's law of Molecular Dissymmetry.

3. The sequence of the rotatory power in the case of salts of *o*-, *m*-, *p*-amino benzoic acids with camphor-β-sulphonic acids in different solvents runs exactly in the reverse order of the dielectric constants of the solvents, whereas the sequence of the rotatory power of salts of *p*-aminoazobenzene with camphor-β-sulphonic acids follows exactly the same order as the dielectric constant of the solvent.

4. The influence of carboxyl group or rotatory power has been discussed and its polar effect on the rotatory power of the compounds traced.

5. The effect of the replacement of H by the azo aryl group is to depress the rotatory power of the parent compound.

6. The effect of position isomerism on rotatory power has also been discussed.

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REFERENCES

1. Singh, B. K., & Manhas, K. M. S. .. *Proc. Ind. Acad. Sci.*, A, 1947, **26**, 61.
——— *et al.* .. *Proc. Lahore Phil. Soc.*, 1944, **6**, 15; *Proc. Ind. Acad. Sci.*, A. 1945, **22**, 84.
2. ——— and Perti, O. N. .. *Proc. Ind. Acad. Sci.*, A, 1945, **22**, 267.
3. Frankland, P. F. .. *Jour. Chem. Soc.*, 1896, **69**, 1583.
Singh, B. K., and Mazumdar, J. K. *Ibid.*, 1919, **115**, 567.
4. Rule .. *Ibid.*, 1924, **125**, 1122.
5. Reychler .. *Bull.*, 1898, (iii), **19**, 120.

SULPHURYL CHLORIDE: A NEW CONDENSING AGENT FOR THE PECHMANN-REACTION. ISOLATION OF TRANS β-2:4-DIHYDROXY-PHENYL-GLUTACONIC ACID

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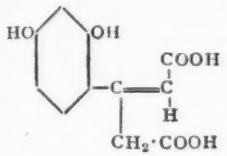
In continuation of our work on the condensation of phenols and phenolic ethers with acetone dicarboxylic acid in the presence of condensing agents other than sulphuric acid, resorcin was condensed with acetone dicarboxylic acid in the presence of sulphuryl chloride, using benzene as solvent. The condensation product was found to contain (i) a non-acidic part and (ii) an acidic part.

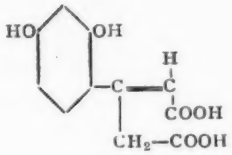
The non-acidic part was identified as the dilactone of ββ-di-(2:4-dihydroxy phenyl) glutaric acid.[1] The acidic part contained two acids A and B which were separated by careful fractional crystallisation from hot water. The former was identified as the 7-hydroxy-coumarin-4-acetic acid. The acid B was obtained as the second crop in the form of pink shining plates (m.p. 195–197° decomp.).

The new acid B titrated as a dibasic acid (eq. wt. 122), gave a dark bluish green coloration with ferric chloride and its alcoholic and alkaline solutions exhibited a fine blue fluorescence. As compared with 7-hydroxy coumarin-4-acetic acid it was more soluble in alcohol and water. When heated at its melting point, it decomposed and gave 4-methyl umbelliferone. On boiling with (i) sodium hydroxide (10%), (ii) sulphuric acid (60%) or (iii) glacial acetic acid, it was largely converted to 7-hydroxy-coumarin-4-acetic acid. A similar change was noticed on heating it at 120–130° for about three hours. It was therefore considered to be the trans isomer (II) of β-2:4-dihydroxy-phenyl-glutaconic acid, since its cis isomer (I) can be obtained only in the form of its sodium salt by the alkaline hydrolysis of 7-hydroxy coumarin-4-acetic acid (III) and not in the free condition due to rapid ring closure. Indeed the spontaneity of lactone formation appears to be the common feature of the cis forms of all β-aryl-glutaconic acids having a –OH group in the ortho position, the only exception being the acid mentioned by Dey[2] as the product of heating β-naphtha pyrone acetic

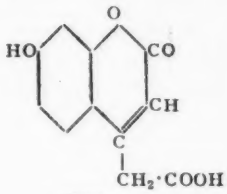
acid with NaOH (20%). There is no case on record, however, in which a β-aryl glutaconic acid with a –OH group in the ortho position has been obtained in the free condition as a product of the condensation between acetone dicarboxylic acid and a phenol.



(I)
(cis)



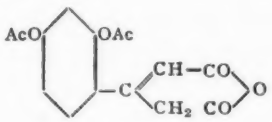
(II)
(trans)



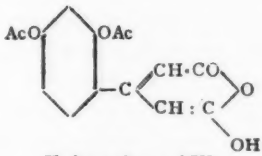
(III)

The new dibasic acid was subjected to the following reactions, for a further elucidation of its constitution:—

1. On refluxing it with acetyl chloride or acetic anhydride, a crystalline powder, m.p. 188°, was obtained. It dissolved slowly in sodium bicarbonate solution, but was titratable as a monobasic acid (eq. wt. 290). In alcoholic solution it gave a greenish black colouration with ferric chloride. On boiling it with NaOH (0·5 N) and acidifying, (i) 7-hydroxy coumarin-4-acetic acid and (ii) the original dibasic acid were obtained. The substance m.p. 188° therefore appeared to be the diacetyl derivative of the expected anhydride (IV). The formation of such titratable anhydrides by the action of acetic anhydride or acetyl chloride is a characteristic of the β-substituted glutaconic acids.[3]



(IV)
Anhydride.

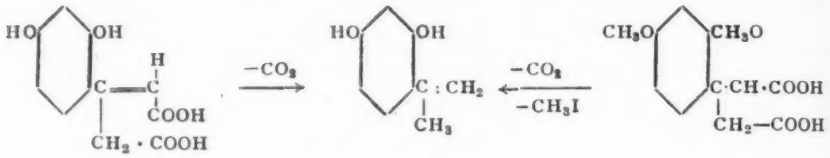


Hydroxy form of IV
(titratable)

Prolonged action of acetic anhydride on the new acid yielded a different compound. It was a white granular powder melting indefinitely over 250° and is being investigated further.

2. Decarboxylation by heating with mineral acids, especially hydriodic acid is yet another characteristic of β-aryl glutaconic acids.[4] The new dicarboxylic acid was refluxed with hydriodic acid (57%) for a few hours. In addition to a small quantity of 4-methyl umbelliferone a non-acidic substance, m.p. 140°, expected to be the 2:4-dihydroxy-isopropylene-benzene (V) was obtained, but reference to literature failed to give further

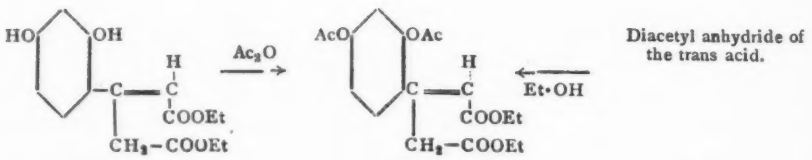
information about this compound for purposes of identification. It was identified therefore with the product obtained by refluxing a sample of the known β-2:4-dimethoxyphenyl glutaconic acid[5] with hydriodic acid.



(II) (V)

3. The new acid was methylated in two ways:—(i) Refluxing a solution of it in acetone with methyl iodide in the presence of a small quantity of anhydrous potassium carbonate,[6] and (ii) by the action of dimethyl sulphate on its alkaline solution. In both cases the acidic product had a m.p. of 178° and was identified with the known β-2:4-dimethoxy phenyl glutaconic acid[5] by mixed melting point and equivalent weight. A considerable quantity of a non-acidic semisolid substance was obtained in the first case. This appeared to be the methyl ester of the above glutaconic acid.

4. The new acid was esterified by passing dry HCl gas through its alcoholic solution at a low temperature (0–5°) and the ethyl ester (VI) melted at 192°. During the esterification a slight conversion of the Trans acid to the Cis form was noticed since a small quantity of the ethyl ester of 7-hydroxy coumarin-4-acetic acid was always found along with the glutaconic ester, m.p. 192° (VI). Despite repeated crystallisations, the glutaconic ester could not be freed from the contamination and hence, a sample pure enough for analysis could not be obtained. The identity of the glutaconic ester, however, was established in two ways; (i) By synthesising it independently by condensing resorcin with ethyl acetone dicarboxylate in the presence of sulphuryl chloride as the condensing agent and (ii) by converting it to its diacetyl derivative m.p. 163° (VII) and identifying the same with the product obtained by boiling the diacetyl derivative of the glutaconic anhydride (IV) with excess of ethyl alcohol.



(VI) (VII) (IV)

Both the glutaconic ester and its acetyl derivative yielded on hydrolysis with dilute NaOH a mixture of (i) 7-hydroxy coumarin-4-acetic acid and (ii) the original trans β-2 : 4-dihydroxy phenyl glutaconic acid.

5. As already mentioned, the trans β-2 : 4 dihydroxy phenyl glutaconic acid was converted to the cis-form which evidently closed the lactone ring and changed to 7-hydroxy coumarin-4-acetic acid by (i) boiling with alkali (5%) or sulphuric acid (60%) or glacial acetic acid, (ii) heating it at its melting point which in turn gave 4-methyl umbelliferone as a result of further decarboxylation of the 7-hydroxy coumarin-4-acetic acid or by heating the glutaconic acid in an air oven at 120–130° for a few hours. A partial conversion was also observed on boiling the acid with alcohol and passing HCl through its alcoholic solution or by heating it with hydriodic acid.

6. Attempts were made to obtain the Trans glutaconic acid directly from its Cis isomer for which the only workable source was 7-hydroxy coumarin-4-acetic acid. Recently Seshadri and his collaborators[7] have worked extensively on the isomerism of coumarinic acids and the problem of their conversion to the coumaric acids and *vice versa* has also been investigated by them in great detail. Working on similar lines the following methods were tried to convert 7-hydroxy coumarin-4-acetic acid into the trans isomer of β-2 : 4-dihydroxy phenyl glutaconic acid :—(i) prolonged boiling with alkali, sodium ethoxide or sodium methoxide,[8] (ii) Action of mercuric oxide or mercuric acetate in alkaline medium[9] (there seemed to be no mercuration in either of these reactions), (iii) action of sodium bisulphite,[10] and (iv) exposure to ultra-violet rays.[11]

None of these methods was successful and in each case the original 7-hydroxy coumarin-4-acetic acid was recovered unchanged. It may be mentioned in passing that these methods of cis-trans conversion have been tried in the case of substituted coumarinic acids, but we have not been able to find a case where any of them has been successfully employed to convert a coumarin acetic acid into the trans isomer of the corresponding glutaconic acid.

Experimental

1. *Trans β-2 : 4-dihydroxy phenyl glutaconic acid.*—

Acetone dicarboxylic acid[1] (15 g.) and resorcin (11 g.) were intimately mixed and suspended in dry benzene (40 c.c.). To this, sulphuryl chloride (8 c.c.) was added in small quantities with shaking. The mixture was allowed to stand for forty-eight hours under a guard tube. After decanting benzene the solid mass was washed with water and treated with sodium bicarbonate solution. The solution was filtered and the non-acidic residue was washed

with warm water and crystallised from alcohol. Small white prismatic crystals that darken at 210° and melt at 290°, yield about 3 g. It was identified as the dilactone of $\beta\beta$-di-(2: 4-dihydroxy phenyl) glutaric acid by mixed melting point and other properties.

The filtrate was acidified and kept overnight in a refrigerator. The solid that separated was filtered, washed and subjected to careful fractional crystallisation from hot water. The first crop (A) came down immediately in the form of long lustrous needles which were quickly separated by filtration, m.p. 203° (decomp.), yield about 2 g. It was identified with an authentic sample of 7-hydroxy coumarin-4-acetic acid by mixed melting point and conversion to 4-methyl umbelliferone, m.p. 182°. The second crop (B) came down from the filtrate slowly in the form of pinkish rhombic plates, m.p. 195–97° (decomp.), yield about 4 g. It was purified by recrystallisation from hot water. Its aqueous solution gave a dark bluish green colouration with ferric chloride and its alcoholic and alkaline solution exhibited a fine blue fluorescence. The formula of trans β-2: 4-dihydroxy phenyl glutaconic acid has been assigned to this substance. (For analysis, the substance was dried in a vacuum desiccator. Found: C, 55·06; H, 4·04 per cent. eq. wt. 122. $C_{11}H_{10}O_6$ requires C, 55·46; H, 4·20 per cent. eq. wt. 119).

On heating the above trans acid (0·5 g.) in a small test-tube at its m.p. in an oil-bath, considerable decarboxylation took place. The residue was washed with sodium bicarbonate solution, filtered and crystallised from alcohol. Pinkish needles, m.p. 182°, were obtained and identified with an authentic sample of 4-methyl umbelliferone. The filtrate on acidification gave a small amount of 7-hydroxy coumarin-4-acetic acid. On prolonged boiling of the trans acid with dilute acetic acid or ethyl alcohol during the process of crystallisation a considerable quantity of 7-hydroxy coumarin-4-acetic acid, m.p. 203° (decomp.), was obtained.

2. *The diacetyl anhydride.*—

(*a*) The trans acid (3 g.) was refluxed with acetyl chloride (25 c.c.) for six hours on a water-bath. The solution was cooled and placed in a desiccator over conc. sulphuric acid for a few hours and filtered through a cotton plug. The filtrate on cooling in an ice-bath and vigorous stirring deposited a white powder which, on separation, drying and crystallisation from acetone, gave a white crystalline powder, m.p. 188°. It gave a bluish green coloration with ferric chloride. It dissolved slowly in sodium bicarbonate solution and titrated as a monobasic acid with alkali (eq. wt. found 291·4; eq. wt. calculated for $C_{15}H_{12}O_7$ is 304).

(*b*) The trans glutaconic acid (3 g.) was heated with acetic anhydride (22 c.c.) on a water-bath for about half an hour. The clear brown liquid was then cooled in an ice-bath with stirring. The white powder that separated was filtered, washed and crystallised from acetone. A white crystalline powder, m.p. 188°, was obtained and found identical with the sample of the diacetyl anhydride described above. Longer heating with acetic anhydride brought about more complex changes that are being studied.

3. *Action of hydriodic acid.*—

The trans glutaconic acid (0·5 g.) was gently boiled with hydriodic acid (6 c.c. of 57%) on a wire-gauze under a long air condenser for about three hours. The mixture was cooled and poured in cold water. The yellow powder, which separated in an hour, was filtered, washed and crystallised from alcohol. The crystals,—pinkish needles were separated, m.p. 179° and identified with 4-methyl umbelliferone. To the red filtrate, obtained after the separation of yellow powder, a solution of sodium thiosulphate was added until the colour of iodine was just discharged. The mixture was then kept in the refrigerator overnight. A small quantity of white powder settled down. It was collected, washed with sodium bicarbonate solution and crystallised from dilute alcohol. Small reddish needles, m.p. 140–42°, were obtained. It gave blue black coloration with ferric chloride. This compound may be regarded as 2: 4-isopropenyl benzene, as it was found identical with the product obtained by the simultaneous decarboxylation and demethylation of the known β-2: 4 dimethoxy phenyl glutaconic acid with hydriodic acid under similar conditions. (Found: C, 71·47; H, 6·15 per cent. $C_9H_{10}O_2$ requires C, 71·97; H, 6·66 per cent.)

4. *Methylation.*—

(*a*) With alkali and dimethyl sulphate: The trans glutaconic acid (1 g.) was dissolved in NaOH solution (20 c.c. of 20%) and methyl alcohol (10 c.c.). Dimethyl sulphate (6 c.c.) was added gradually with shaking and the mixture refluxed for two hours. A further quantity of NaOH solution (10 c.c.) of (20%) was added and the mixture refluxed again for an hour. It was cooled, diluted and filtered. The filtrate on acidification gave an yellow acidic product, which was dissolved in $NaHCO_3$ and reprecipitated by acidification. It was crystallised from dilute alcohol. Small yellow prisms, m.p. 178–80° (decomp.). This was identified as β-2: 4-dimethoxy phenyl glutaconic acid, by mixed m.p. and equivalent weight (eq. wt. found 132·8; $C_{13}H_{14}O_6$ requires eq. wt. 133.0).

(*b*) With methyl iodide: The trans glutaconic acid (0·5 g.) was dissolved in dry acetone (50 c.c.). To this anhydrous K_2CO_3 (2g., and methoxyl

iodide (6 g.) were added and the mixture refluxed on a water-bath for about forty-eight hours under a long spiral condenser, protected by a guard tube. About 5 g. of methyl iodide was further added during heating to make up for the loss due to evaporation. The mixture was cooled and filtered, the solid on the filter being repeatedly washed with acetone. The filtrate was evaporated, which deposited a sticky yellowish mass. This was dissolved in $NaHCO_3$ solution and after shaking with ether, reprecipitated by acid. On crystallisation from alcohol it gave yellowish prisms, m.p. 178° (decomp.), yield about 0·2 g. It was identified with β-2: 4-dimethoxy phenyl glutaconic acid as before. On evaporating the ether extract slowly a thick liquid was left behind. This appeared to be the dimethyl ester of the trans glutaconic acid.

5. *Diethyl ester.*—

(*a*) The trans glutaconic acid (2 g.) was dissolved in dry absolute alcohol (40 c.c.). Dry HCl gas was passed through this solution, which was cooled in ice, for about two hours. After some time, short white needles settled down. These were collected, washed with $NaHCO_3$ solution and recrystallised several times from absolute alcohol, m.p. 190°; yield about 1 g.

(*b*) Ethyl acetone dicarboxylate (11·8 g.) and resorcin (5·2 g.) were dissolved in dry benzene (10 c.c.). Sulphuryl chloride (8 c.c.) was added slowly to this mixture. A reddish brown mixture resulted, which was allowed to stand for forty-eight hours under a condenser with guard tube. A white crystalline solid was deposited. The supernatant liquid on evaporation gave some more quantity of the white crystalline substance. It was crystallised from alcohol several times. Yield about 3 g., m.p. 190°. It was found identical with the ester described above. However, the samples in both cases were found contaminated with traces of the ethyl ester of 7-hydroxy coumarin-4-acetic acid, which could not be removed in spite of all attempts and hence the analytical results were approximate. The substance is regarded as the diethyl ester of the trans β-2: 4-dihydroxy phenyl glutaconic acid.

6. *Diacetyl derivative of the diethyl ester.*—

(*a*) The diethyl ester described above (1 g.) was dissolved in acetic anhydride (10 c.c.) and refluxed for 2 hours. It was poured on ice and kept standing for some time. The white solid product was crystallised from alcohol. White flaky plates, yield about 1 g., m.p. 163°.

(*b*) The diacetyl anhydride of the trans β-2: 4-dihydroxy phenyl glutaconic acid (0·5 g.) was boiled with absolute alcohol (20 c.c.) for 4 hours

and the mixture was poured in a large excess of ice-water. The white product that separated was washed with $NaHCO_3$ solution and crystallised from alcohol. White flaky plates, yield about 0·5 g., m.p. 162°. This was found identical with the above derivative by mixed melting point. The $NaHCO_3$ washings gave on acidification an acidic substance, which appeared to be the acid ethyl ester (*i.e.*, mono ethyl-ester) of the trans β-2: 4-dihydroxy phenyl glutaconic acid and is being investigated further.

7. *Trans–Cis conversion.*—

(*a*) The trans glutaconic acid (about 1 g.) was refluxed with NaOH solution (20 c.c. of 10%) for one hour, cooled, filtered and acidified. The white precipitate was separated and crystallised fractionally from hot water. The first major crop (about 0·6 g.) consisted of long lustrous needles, m.p. 203° (decomp.) and was found identical with 7-hydroxy coumarin-4-acetic acid. The small second crop consisted of the unchanged trans glutaconic acid.

(*b*) On heating the trans glutaconic acid (0·5 g.) either with sulphuric acid (60% 10 c.c.) or with glacial acetic acid for one hour on a water-bath and diluting the solution with water a white precipitate was obtained. This on crystallisation gave 7-hydroxy coumarin-4-acetic acid, m.p. 203° (decomp.) and a small quantity of the unchanged original glutaconic acid.

(*c*) On heating the trans acid in an air oven at 120–30° for about 4 hours it changed completely to 7-hydroxy coumarin-4-acetic acid. The results of ultimate analysis agreed with the formula of Trans β-2: 4-dihydroxy phenyl glutaconic acid before heating and with that of 7-hydroxy coumarin-4-acetic acid after heating.

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SUMMARY

Resorcin has been condensed with acetone dicarboxylic acid in the presence of sulphuryl chloride as the condensing agent. A new dibasic acid has been isolated from the condensation product. In view of the results obtained by submitting the new acid to several reactions it is considered to be the trans isomer of β-2: 4-dihydroxy phenyl glutaconic acid.

References

1. Dixit, Kankudti and Mulay — *J. Ind. Chem. Soc.*, 1945, **23**, 207.
2. Dey .. *J. C. S.*, 1915, 1606.
3. Limaye and Bhave .. *J. Ind. Chem. Soc.*, 1931, **8**, 137.
4. Gogte .. *Proc. Ind. Acad. Sci.*, 1935, **1 A**, 185.
   Limaye and Bhave .. *J. Ind. Chem. Soc.*, 1931, **8**, 137.
5. Bawdekar .. *M.Sc. Thesis* to Univ. Bom., 1942.
6. Rao, Reddy and Seshadri *Proc. Ind. Acad. Sci.*, 1941, **12 A**, 495.
7. Dey, Rao and Seshadri .. *J. Ind. Chem. Soc.*, 1934, **11**, 743.
   Seshadri and Suryaprakasa-rao *Proc. Ind. Acad. Sci.*, 1936, **3 A**, 293; **4 A**, 157.
   Rangaswami and Seshadri *Ibid.*, 1937, **5 A**, 249.
   Rao, Rao and Seshadri .. *Ibid.*, 1937, **6 A**, 148.
   Murty, Rao and Seshadri *Ibid.*, 1937, **6 A**, 316.
8. Biilmann .. *Ann.*, 1912, **388**, 259.
9. Sen and Chakravarti .. *J. Ind. Chem. Soc.*, 1929, **6**, 849; 1930, **7**, 247.
10. Dodge .. *J. Am. Chem. Soc.*, 1916, **38**, 450.
    Dey and Row .. *J. C. S.*, 1924, 554.
11. Stoermer .. *Ber.*, 1909, **42**, 4865.
    Neogi and Chatterji .. *J. Ind. Chem. Soc.*, 1928, **58**, 279.

OPACITY CHANGES DURING THE SOL-GEL TRANSFORMATION OF SOAP-PINENE SYSTEMS

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Prasad *et al.*[3] have investigated systematically the opacity changes taking place during the sol-gel transformation of several inorganic gel-forming systems. In their earlier work, they determined the extinction coefficients of gel-forming systems, but later they measured the changes in opacity using either a thermopile or an amplified photo-cell unit, and more recently by using a compensated photo-electric arrangement in which all possible errors are avoided. Their extensive studies have shown that there are two types of gels, (i) those that increase, and (ii) those that decrease, in opacity, during gelation. The changes in opacity taking place during gelation have been attributed by them to changes in the size, shape and state of aggregation of the gel particles during the formation of gels.

The intensity of light scattered by gel-forming solutions of gelatin and agar-agar, and the extent to which it is depolarized, have been investigated by Krishnamurthy,[1] using incident light unpolarized. He finds that the particles in the gel state are bigger and/or greater than those in the sol state. Prasad and Guruswamy[4] have investigated the intensity and depolarization factors of scattered light using unpolarized, and horizontally and vertically polarized light, during the sol-gel transformation of several inorganic gel-forming substances in water, and report a continuous increase in micellar size with progress of gelation, the increase continuing in some cases even after the gel had set.

The effects of various factors which influence the process of gel-formation have been studied by Mardles[2] who has measured the changes in the Tyndall Number during the sol-gel transformation of cellulose acetate in benzyl alcohol. He finds that the curves obtained on plotting the Tyndall Number against the concentration rise at first, reach a maximum, and then fall, the peak of the curve indicating the existence of an optimum concentration at which maximum particle size is obtained. Similar maxima are revealed in the curves of Tyndall Number against temperature.

Gels of alkali soaps in pinene were prepared for the first time by Prasad *et al.*, and the results of their investigations on several properties of these gels have been published in a series of papers in the *Proceedings of the Indian Academy of Sciences*.[5, 6] The opacity changes taking place during the gel-formation of these soap-pinene systems have been investigated by the author with a view to determining the mechanism of formation of these gels, as also the manner in which the size, number and degree of solvation of the colloidal particles change during setting.

Materials Used

Sodium oleate and sodium palmitate used were pure products of the B. D. House, whereas sodium stearate was obtained from Messrs. E. Merck & Co; pinene was a product of Messrs. Eastman Kodak & Co., and was the fraction distilling at 156° C.

Experimental Technique

The opacity measurements were made by means of a Klett-Summerson glass-cell photo-electric colorimeter. A projection-type electric lamp (100 watts; 230 volts) fitted with a blue filter (400 to 465 millimicrons) was used as the source of light, and the current produced by the photo-cells was measured by means of a suspension-wire type glavanometer. The opacity or intensity of transmitted light was measured in terms of the divisions on the potentiometer slide-wire which are necessary to nullify the torsion applied to the galvanometer needle. The instrument was found to yield results of considerably high accuracy; several observations, taken with the same system under identical conditions, did not differ by more than $\pm$ 0·3 per cent. These results therefore represent fairly accurately the changes in opacity which take place in the gel-forming systems during setting.

The experimental procedure adopted was as follows: the instrument was corrected for the zero error and the galvanometer needle brought to the zero position. Gel-forming solutions containing different known amounts of a soap in 10 c.c. of pinene were prepared, as described by Prasad and Hattiangdi,[5] in the glass-cell, provided with the instrument, which was then immediately placed in position. The lamp was switched on and the opacity values were determined at successive known intervals of time until the system attained a constant value of opacity at the room temperature (30° C.).

The results obtained for systems containing different amounts of sodium oleate and sodium stearate are presented graphically in Figs. 1 and 2 in which the values of opacity are plotted against time.

Discussion of Results

It will be noticed from the data presented in Figs. 1 and 2 that the values of opacity increase with time during the setting of sodium oleate and sodium stearate gels. It was found that the opacity of systems containing 0·045 g., 0·055 g., and 0·065 g. of sodium palmitate did not change at all with time throughout the process of gel-formation. This anomalous behaviour is due to the fact that whereas the former two soaps dissolve in pinene to give clear mobile solutions, sodium palmitate does not dissolve completely even at the boiling point of pinene. The latter exists as a sufficiently viscous system, and on cooling it, the fairly solvated aggregates of soap particles which are dispersed in this system, coalesce and set to a gel; hence, its opacity does not undergo any change during the process of gel-formation.

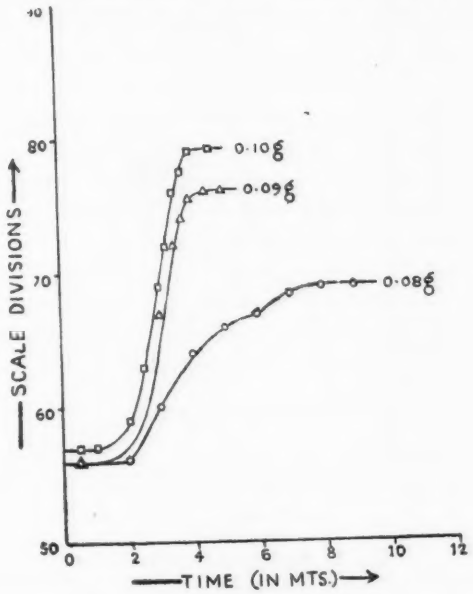

Fig. 1. Sodium Oleate in Pinene

The various opacity-time curves in Figs. 1 and 2 rise very slowly at first, then very rapidly and once again very slowly to reach an almost constant value of opacity. At this stage, for systems containing 0·08 g. of the soap, the curves rise sufficiently rapidly once again and later on tend to run parallel to the time axis. The general nature of the latter curves is thus different from the S-shaped curves reported by previous workers.

The nature of the various opacity-time curves can be explained as follows: Prasad *et al.*[6] have found that sodium oleate and sodium stearate form true solutions in pinene at its boiling point and that they exist in this state until the temperature has fallen down to about 110° C. or a little lower. The approximate constancy in the initial opacity values is due to the fact that the absorption of light by true molecular solutions does not change unless saturation or suspended particles interfere. Even if primary colloidal particles are formed during this period of initial cooling, their size as well as their number will be extremely small, and hence the opacity values will not be affected appreciably.

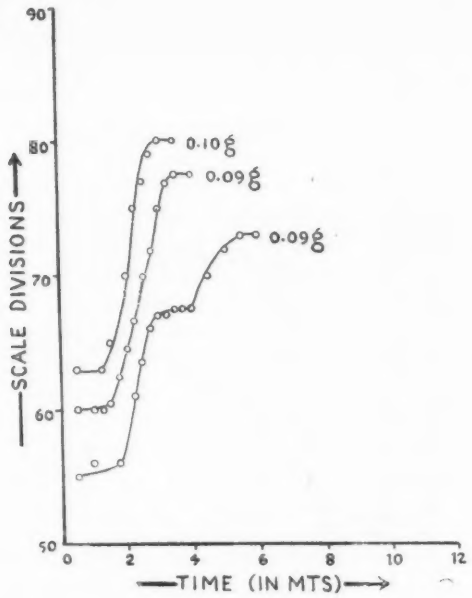

FIG. 2. Sodium Stearate in Pinene

Further cooling of these solutions increases their degree of super-saturation and causes the formation of a number of colloidal particles. An increase in the size and number of these particles brings about the observed rapid rise in opacity with time which persists until both the size and the number of the particles have reached almost the maximum value. After this period, the particles take up plenty of the dispersion medium and the micelles become heavily solvated. During this process of solvation, the changes in the intensity of the scattered light are not large for reasons of

refractive index, and hence the opacity increases rather slowly to reach almost a constant value; this is indicated by the portion of the curve which tends once again to run parallel to the time axis. This period was found to coincide approximately with the setting time of the gel system determined by other methods.

The peculiar behaviour exhibited by systems containing 0·08 g. of sodium oleate and sodium stearate, that is the sudden change in the direction of the curves, is very interesting and is caused probably by the structural changes which take place in these set gels on further cooling. The curves show that these changes are rapid at first, and then slow down until a final structure is formed. It is not very easy to visualise as to how these structural changes actually take place. However, in view of the fact that these gels set at a temperature much higher than the room temperature, it can be surmised that the structural changes are brought about on account of the separation of the soap from the state of solution or suspension which exists either in the intermicellary or in the inter-fibrillary liquid.

It is evident from the several curves in Figs. 1 and 2 that as the soap content of the gel-forming systems is increased, (i) the changes in opacity take place at a quicker rate and the final constant value is obtained earlier, and (ii) the change in direction of the curves after the S-shaped portion has been completed, which is predominant at lower concentrations, appears to flatten out and is not noticeable. This may be due to the fact that in the case of gels of larger soap content, the rate of the structural changes in these gels, or in other words the rate of growth of the particle size, after the setting point has been reached is the same as that prior to gelation.

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Summary

Measurements of the opacity changes with time taking place during the gel-formation of some soap-pinene systems yield opacity-time curves which change their nature considerably with variations in concentration. The curves obtained for systems of high concentrations are S-shaped whereas those for low soap content show a distinct change in direction after the S-shaped stage is reached. The curves for sodium oleate and sodium stearate gels in pinene are very similar in their general characteristics but the opacity values for the sodium palmitate-pinene systems remain constant

throughout the process of gel-formation. An attempt has been made to correlate the data with the manner in which the size, number and degree of solvation of the colloidal particles change during gelation.

References

1. Krishnamurthy .. *Proc. Roy. Soc.*, 1929, **122 A**, 76.
2. Mardles .. *Trans. Farad. Soc.*, 1923, **18**, 365.
3. Prasad *et al.* .. *J. Indian Chemical Soc.*, 1929, **6**, 653 ; *J. Phys. Chem.*, 1932, **36**, 1324 ; *Proc. Ind. Acad. Sci.*, 1943, **17**, 161 ; 1944, **19**, 389.
4. Prasad & Guruswamy .. *Proc. Ind. Acad. Sci.*, 1944, **19**, 47, 66, 77.
5. Prasad & Hattiangdi .. *Ibid.*, 1945, **21**, 1.
6. Prasad, Hattiangdi, *et al.* .. *Ibid.*, 1945, **21**, 56, 90, 105 ; 1946, **24**, 287, 295.

SAMARSKITE FROM NELLORE DISTRICT

Part II. Chemical Composition

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Introduction

In Part I[1] it was pointed out by the authors that Tipper's identification of the mineral, Samarskite, occurring in the Nellore District was based only on its megascopic characters and qualitative analyses carried out by Blyth. It was shown that Samarskite occurs often closely intergrown with Columbite-Tantalites. The Uranium and "Earth Acid" contents of a number of samples were reported.

The object of the present paper is to report on the chemical composition of a typical sample of samarskite. The specimen chosen weighed about 820 gm. It has indistinct crystal faces developed on one side but is mostly irregular, massive and partially intergrown with felspar. The latter is also seen as fine veins shot through the samarskite. These, however, are quite superficial. The mass appears otherwise perfectly homogeneous. The specimen was cut through and the cut surfaces polished. There was no evidence of intergrowth with any other mineral as noticed in some other specimens of samarskite from the same area.[1] Autoradiographs of the polished specimens using ordinary photographic plates also failed to detect any lack of homogeneity in the specimen. The general physical properties of the specimen are as follows: Colour, Velvet black; Streak, Dark brown; Lustre, Vitreous and splendent; Hardness, about 6; and Specific gravity, 5·625.

It is well known that the rare earth minerals always contain a number of rare earths in varying proportions. The points of special interest in the analytical study of samarskite are: (*a*) the thorium content, (*b*) the presence of cerium, (*c*) uranium in the quadrivalent and hexavalent states, and (*d*) the lead content.

Thorium is not one of the rare earths but is generally associated with them. Spencer[2] states that it is quite probable that many of the rare earth minerals in which thorium has not been reported, do actually contain it, although in very small quantities, for the rare earths may be regarded as

the ultimate disintegration products of thorium. The thorium content is also of interest in the calculation of the age of the mineral.[3] J. L. Smith,[4] and Allen,[5] do not report any thoria in their samples of samarskite from North Carolina, but others report amounts varying from 1·73 to 6% as shown in the table below (Spencer, *loc. cit.*).

Authors	Source of Samarskite	ThO_2%
Finkener and Stephans ..	Minsk	6·0
Hillebrand ..	Colorado	3·64
Chroustschoff ..	Urals	1·73

Smith (*loc. cit.*) did not find any cerium in N. Carolina samarskite while Allen (*loc. cit.*) reported a minute quantity, and Wells[6] found 0·2% cerous oxide in a sample presumably of American origin.

Uranium occurs both in the quadrivalent and hexavalent states in samarskite and these can be separated as the insoluble green uranous and the soluble uranyl fluorides, using hydrofluoric acid (J. L. Smith's method), but it is doubtful, as pointed out by Wells (*loc. cit.*) if the results obtained represent the composition of the mineral exactly. The actual content of uranium is of interest in the calculation of the age of the mineral as well as the radium content (*cf.* Part I).

The lead content enters into the calculation of the age of the mineral but its accurate determination is considerably difficult. The possible presence of lead of non-radioactive origin in the mineral itself as well as lead in the reagents used, vitiates the results. Further, unless the specimen is fresh and unaltered, the figure is of no value.

Chemical Analysis

Chemical analysis was carried out on the same general lines as in the J. L. Smith method (*loc. cit.*) involving the decomposition of the mineral with hydrofluoric acid. The insoluble portion contains mainly the rare earths and quadrivalent uranium while the soluble portion contains the "Earth Acids", hexavalent uranium, iron and manganese. Minor constituents such as tin, tungsten and titanium go exclusively with the "Earth Acids" while lead, calcium and magnesium are found mostly in the insoluble portion. This separation into two groups is not clean cut as can be seen from the data given by Wells (*loc. cit.*).

Actual analysis was carried out according to Girotto's[7] procedure modified suitably as follows:—(*a*) thorium was separated and estimated by the

hexamine method,[8] (*b*) cerium isolated by the iodate method and estimated by ignition to ceria by way of the oxalate,[8] (*c*) the cerium and yttrium group of earths were separated by the double sulphate method using potassium sulphate and independently estimated by conversion to oxalates and ignition to the oxides,[8] and (*d*) the major portion of the "Earth Acids" was precipitated directly by dilution and boiling while the rest was recovered from the filtrate by the tannin method from alkaline tartrate solution after removal of iron as sulphide.[8]

Results

All the major constituents of the specimen were determined. The results obtained are reported in Column I in the following table:—For comparison results obtained by Smith, Miss Swallow and Allen are also reported in Columns II, III and IV respectively (*cf.*, Smith, *loc. cit.*).

	I	II	III	IV
1 Earth acids ..	57·4	55·13	54·96	55·8
2 Thoria ..	1·98	..	..	..
3 *Cerium Earths*: ..	(1·2)	4·24	5·17	4·25
(*a*) Ceria ..	0·4	..	..	..
(*b*) Lanthanum Earths ..	0·8*	..	..	..
4 Yttria Earths ..	16·9*	14·49	12·84	14·45
5 UO_2 ..	8·4	10·96	9·91	12·46
6 UO_3 ..	Nil			
7 FeO ..	9·1	11·74	14·02	10·90
8 PbO ..	2·25†	..	..	..
9 CaO ..	1·1	..	..	0·55
10 Loss on ignition ..	0·87	0·72	0·52	1·12
11 MnO ..	..	1·53	1·09	0·75
12 MgO ..	..	Trace	..	..
13 WO_3 ..	..	0·31	0·16	0·08
14 SnO_2 ..	..			
15 ZrO_2 ..	..	..	..	..
16 TiO_2 ..	..	..	..	..
17 Insoluble residue from "Cerium oxides"	..	..	1·25	..
Total ..	99·20	99·12	99·72	100·36

* Uncorrected for peroxidic oxygen.

† This value is unreliable as lead-free reagents could not be secured.

Several attempts to precipitate hexavalent uranium, if any, from the H. F.-soluble portion by the usual procedure failed to yield the yellow ammonium diuranate and hence it must be presumed that either hexavalent uranium is absent or is present in minute quantity. Other points of interest are the presence of 1·98% thoria and 0·4% ceria.

Calculation of Radium content according to the formula of L.D. Roberts.[9]

$U\% \times 3{\cdot}4 = \text{mg. Ra. per ton.}$

$7{\cdot}406 \times 3{\cdot}4 = 25{\cdot}19$ mg. Radium per ton.

i.e., 1 gr. in 39·71 tons.

It is nearly as rich as the Katanga Carnotite.[10]

Summary

1. A typical sample of samarskite has been analysed and the results reported.

2. The thoria content of the sample is 1·98%.

3. The percentage of cerium earths present in this sample is relatively much smaller than found in samples from North America. Our sample contains 0·4% ceria.

4. Hexavalent uranium has not been found in the sample but this is of no special significance.

5. The radium content is 1·0 gr. in 39·71 tons and the Nellore samarskite is nearly as rich as Katanga Carnotite in this element.

References

1. Karunakaran and Neelakantam — *Proc. Ind. Acad. Sci.*, 1947, **25 A**, 404.
2. Spencer .. *The Metals of the Rare Earths*, 1919, 13.
3. .. *Physics of the Earth*, 1931, **4**, 99.
4. J. L. Smith .. *Am. J. Sci.*, 1877, **13**, 359.
5. Allen .. *Ibid.*, 1877, **14**, 128.
6. Wells .. *J. Am. Chem, Soc.*, 1928, **50**, 1017.
7. Girotto .. *Chemical Abstracts*, 1941, 3557.
8. Schoeller and Powell .. *The Analysis of Minerals and Ores of the Rarer Elements*, 1940.
9. L. D. Roberts Scott .. *Standard Methods of Chemical Analysis*, 1939, **1**, 767.
10. Karunakaran and Neelakantam — *J. Sci. Ind. Res.*, 1946, **5 B**, 36.

INSECTICIDAL PROPERTIES AND CHEMICAL CONSTITUTION

Part. IV. Some Simple Chromones and Isoflavones

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In Part II[1] it was pointed out that there exists a marked difference between the toxic properties of the simpler coumarins and the simpler flavones and this was attributed to the absence of the side phenyl nucleus in the former. A study of 3-phenyl- and 4-phenyl-coumarin derivatives gave ample support to this idea since they were found to be comparable in toxicity with the flavone derivatives. Another way of proving this point would be to examine simpler chromones which do not have the side phenyl nucleus. This has now been done and they are found to be feebly toxic (Nos. 1–3 in the table).

In the skeleton of rotenone and other rotenoid molecules, the side phenyl nucleus is attached to the 3-position of the pyranone ring. Consequently iso-flavones should have greater structural resemblance to them than flavones. Hence a few simple compounds of the isoflavone group have now been tested (Nos. 7–11). The hydroxy compounds appear to be more toxic than the corresponding flavones whereas the methoxy compounds are less toxic. In this respect isoflavones resemble the phenylcoumarins.[1]

Data presented in Part III[2] indicated that the presence of a free hydroxyl in the 5-position of flavones is an advantage in some cases. The chief difficulty in their study by employing the fish technique is their sparing solubility in aqueous medium. 5-Hydroxy-7-methoxy-2-methyl-isoflavone (10) is found to be more toxic than even the corresponding dimethoxy compound (11). The simple 5-hydroxy flavone (4) itself has been tested now. It could be employed only in a concentration of 10 mg. per litre and is found to be ineffective. Since in the coumarin group 5-methoxy-4-methyl-coumarin was found to be definitely more toxic than the isomeric 7-methoxy-compound, 5-methoxy-flavone (5) has been examined. It is however found to be much less toxic as compared with 7-methoxy-flavone.

A number of allyl derivatives (12–20) belonging to the chromone, flavone and isoflavone groups have also been tested. The simpler 7-allyloxy-compounds are even somewhat better than the corresponding methyl ethers. But the effect of the further presence of a nuclear allyl group in the 8-position is not uniform. In the chromone this seems to be an advantage whereas in the flavone it is a disadvantage. 8-Allylated-7-hydroxy compounds are uniformly weak, but the methylation of these compounds re-establishes the toxicity. In regard to these allyl compounds it should be remarked that besides the rapidity with which they bring about toxic effect, they seem to cause more permanent injury than the methyl ethers since the recovery of the fish after transfer to fresh-water is markedly slower and poorer. Hence some of these may prove to be useful insecticides.

The following table gives a summary of the results.

TABLE

ge = gelatin added

	Compound	Concentration in mg. per litre	Turning time
1	2-Methyl-7-hydroxy-chromone ..	100	No action in 24 hours
2	2-Methyl-3-methoxy-7-hydroxy chromone ..	50	,,
3	2-Methyl-7-methoxy-chromone ..	100	18·0 min.
		80	41·0 ,,
4	5-Hydroxy-flavone[3] ..	10	No action in 18 hours
5	5-Methoxy-flavone[3] ..	20 (ge)	10 min.
		10 do	34·5 ,,
6	5:7-Dimethoxy-flavone[5] ..	30 do	9·0 ,,
		20 do	13·5 ,,
7	7-Hydroxy-2-methyl-isoflavone ..	30 do	21·5 ,,
8	7-Methoxy-2-methyl-isoflavone ..	20 do	5·0 ,,
		10 do	20·0 ,,
9	5:7-Dihydroxy-2 methyl-isoflavone ..	50 do	6·5 ,,
		20 do	18·0 ,,
10	5-Hydroxy-7-methoxy-2-methyl-isoflavone ..	12·5 do	7·0 ,,
		10 do	16·0 ,,
11	5:7-Dimethoxy-2-methyl-isoflavone ..	30 do	9·0 ,,
		20 do	15·0 ,,
12	7-Allyloxy-2-methyl 3-methoxy-chromone[4] ..	20 do	No action in 18 hours
		40 do	18·5 min.
		50 do	11·0 ,,
13	7-Allyloxy-8-allyl-2-methyl-3-methoxy-chromone[4]	20 do	6·0 ,,
		10 do	12·5 ,,
14	7-Allyloxy-flavone[4] ..	10 do	4·0 ,,
		5 do	7·5 ,,
15	7-Hydroxy-8-allyl-flavone[4] ..	10 do	No action in 12 hours
16	7-Allyloxy-8-allyl-flavone[4] ..	10 do	5 hours 50 min.
17	7-Methoxy-8-allyl-flavone ..	20 do	6·5 ,,
		10 do	8·5 ,,
		5 do	17·0 ,,
18	7-Allyloxy-2-methyl-isoflavone ..	20 do	4·0 ,,
		10 do	9·0 ,,
19	7-Hydroxy-8-Allyl-2-methyl-isoflavone ..	10 do	No action in 2 hours
20	7-Methoxy-8-allyl-2-methyl-isoflavone ..	10 do	4·0 min.
		5 do	5·5 ,,

Experimental

7-Methoxy-2-methyl-isoflavone

7-Hydroxy-2-methyl-isoflavone was prepared by the method of Baker and Robinson.[6] Its methylation could be conveniently effected in dry acetone medium using excess of dimethyl sulphate and anhydrous potassium carbonate and boiling for 8 hours. The solvent was then removed by evaporation and water added to the residue. The precipitated solid was filtered, washed with water and crystallised from alcohol. It was obtained as glistening needles melting at 135–36°.

7-Allyloxy-2-methyl-isoflavone

7-Hydroxy-2-methyl-isoflavone (2·3 g.) was dissolved in anhydrous acetone (75 c.c.) and treated with allyl bromide (1·5 c.c.) and anhydrous potassium carbonate (3 g.). The mixture was refluxed for 8 hours and then the solvent removed by evaporation. Water was added to the residue and the precipitated solid filtered and washed with water. It crystallised from aqueous alcohol in the form of colourless rectangular prisms and plates melting at 107–108°. Yield 2·6 g. (Found: C, 77·8; H, 6·5; $C_{19}H_{16}O_3$ requires C, 78·1 and H, 6·9%.)

8-Allyl-7-hydroxy-2-methyl-isoflavone

7-Allyloxy-2-methyl-isoflavone (0·5 g.) was heated at 220–30° for 3 hours under reduced pressure. The product was then taken up in ether and extracted thrice with 5% aqueous sodium hydroxide. When the extract was acidified with hydrochloric acid, the 8-allyl derivative was precipitated as a colourless solid. It was sparingly soluble in alcohol and crystallised from alcohol-acetic acid mixture in the form of stout rhombohedral prisms and plates melting at 256–58°. Yield 0·3 g. (Found: C, 78·4; H, 6·4; $C_{19}H_{16}O_3$ requires C, 78·1 and H, 6·9%). Some unchanged 7-allyloxy 2-methyl isoflavone (0·1 g.) was recovered from the ether layer left after alkali extraction.

8-Allyl-7-methoxy-2-methyl-isoflavone

The methylation of the above compound (0·5 g.) was carried out in acetone solution with dimethyl sulphate and anhydrous potassium carbonate. The methyl ether crystallised from aqueous alcohol as long rectangular rods and prisms melting at 144–45.° Yield, 0·3 g. (Found: C, 78·8; H, 5·9; $C_{20}H_{18}O_3$ requires C, 78·4 and H, 5·9%).

The methylation of 7-hydroxy-8-allyl-flavone was similarly carried out and *7-methoxy-8-allyl-flavone* obtained in good yield, m.p. 149–50°.

7-Methoxy-5-hydroxy-2-methyl-isoflavone

This was prepared earlier by Baker and Robinson[6] by methylating 5:7-dihydroxy-2-methyl-isoflavone with dimethyl sulphate and aqueous alkali. This partial methylation has now been effected conveniently with dimethyl sulphate and potassium carbonate in acetone medium.

A solution of the dihydroxy-isoflavone (0·5 g.) in anhydrous acetone (50 c.c.) was treated with dimethyl sulphate (0·3 g., 1·1 mol.) and anhydrous potassium carbonate (1·5 g.). The mixture was refluxed for 10 hours. The solvent was distilled off and water added. The precipitated solid was collected and crystallised from alcohol. It was obtained in the form of glistening colourless needles melting at 185–86°. Yield, 0·4 g.

5:7-Dimethoxy-2-methyl-isoflavone

5:7-Dihydroxy-2-methyl-isoflavone (0·5 g.) was methylated as before with excess of dimethyl sulphate and anhydrous potassium carbonate in acetone solution. It crystallised from aqueous alcohol (animal charcoal) as colourless rectangular plates and rods melting at 105–7°. Yield, 0·4 g. (Found: C, 69·1; H, 5·9; $C_{18}H_{16}O_4$, H_2O requires C, 68·8; H, 5·7%).

Chrysin-dimethyl ether (*5:7-dimethoxy flavone*) has also now been prepared by the above method. It was originally obtained by synthesis[5] from 4:6-dimethyl ether of phloracetophenone by the Baker-Venkataraman method. Earlier attempts to methylate chrysin yielded only the monomethyl ether, tectochrysin. The dimethyl ether melted at 143° and did not dissolve in alkali nor give any colour with ferric chloride.

Summary

The simpler chromones having no side phenyl ring have poor toxic properties and resemble the simpler coumarins. Hydroxy isoflavones are more toxic than the corresponding flavones and the methoxy derivatives less toxic. In this there is resemblance to the hydroxy- and methoxy-phenyl coumarins. Among allyl-derivatives of chromones, flavones and isoflavones, ethers have high toxicity.

References

1. Murti and Seshadri .. *Proc. Ind. Acad. Sci.*, 1947, **25A**, 333.
2. Seshadri and Viswanadham *Ibid.*, 1947, **25A**, 337.
3. Rajagopalan, Rao and Seshadri *Ibid.*, 1947, **25A**, 432.
4. Rangaswami and Seshadri .. *Ibid.*, 1939, **9**, 1.
5. Gulati and Venkatraman .. *J. C. S.*, 1936, 268.
6. Baker and Robinson .. *Ibid.*, 1925, 1984; 1929, 160.

NUCLEAR OXIDATION IN THE FLAVONE SERIES

Part VIII. 7: 8-Dihydroxy-Flavone and -Flavonol

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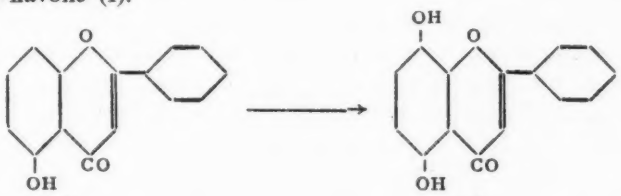
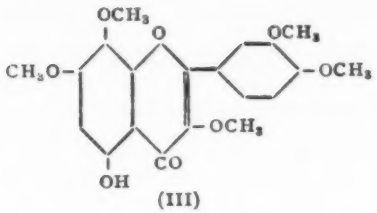
In the large number of nuclear oxidations with alkaline persulphate published earlier in this series of papers[1] the new hydroxyl group entered the 8-position which is para to the already existing and activating hydroxyl group in the 5-position. The simplest example is the preparation of primetin (II) from 5-hydroxy-flavone (I).



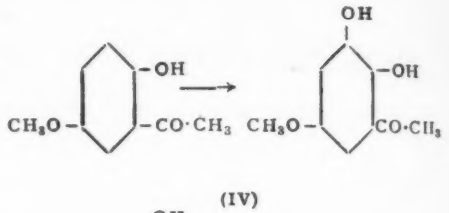
(I) (II)

Ortho oxidation was attempted with gossypetin-pentamethyl-ether (III); but it was not successful. The ortho position 6 was not appreciably affected. But Baker *et al.*[2] have reported that in a simpler case of a phenolic ketone (IV) oxidation in the ortho-position does occur, though the yield is extremely small (1%). With the idea of testing the feasibility of ortho-oxidation in the flavone series in the most favourable case the oxidation of 7-hydroxy-flavone has now been examined. In 7-hydroxy-chromones, flavones and coumarins the 8-position is fairly readily reactive as regards nitration, bromination, Claisen and Fries migrations. Hence this 8-position could be expected to undergo oxidation fairly easily. Further the simplicity of the compound is an advantage for the purpose of the test. Actually it is found that the oxidation of 7-hydroxy-flavone does take place though the yield (10%) is poor as compared with the para oxidations. The product has been identified as 7: 8-dihydroxy-flavone (VI) by comparison with an authentic sample, prepared from gallacetophenone.[3] The acetates and methyl ethers are also found to be identical.

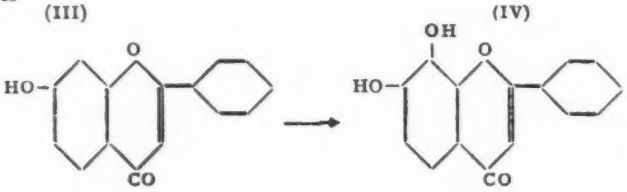
In carrying out the above oxidation several times an observation has been made which is of some significance. After completing the oxidation



(III)

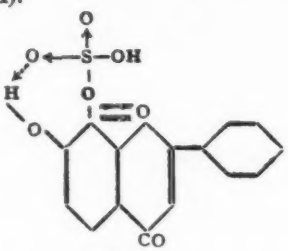


(IV)



(V) (VI)

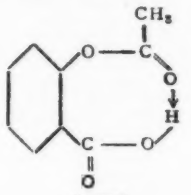
and removing the unchanged substance, the solution is strongly acidified with cooling and allowed to stand for a few minutes when a crystalline precipitate separates out. It is fairly readily soluble in water and alcohol and insoluble in ether and contains sulphur. It gives a brownish pink colour with alcoholic ferric chloride whereas 7-hydroxy-flavone gives no colour and 7 : 8-dihydroxy-flavone a deep green colour characteristic of the catechol structure. Further the precipitate when hydrolysed with hydrochloric acid gives the test for sulphate and yields 7 : 8-dihydroxy-flavone. It has the composition corresponding to the monosulphate of 7 : 8-dihydroxy-flavone. It thus proves to be the intermediate stage in the persulphate oxidation mentioned in the first paper of this series[1] and not so far isolated in other cases. Its successful isolation in this particular oxidation should be attributed to its sparing solubility. This property and its colour reaction with ferric chloride suggest similarity with ortho hydroxy carbonyl compounds which are known to be chelated. The structure of the sulphate could therefore be represented as in (VII).



(VII)

This would involve a chelate ring of 7 atoms. Though chelate rings with 6 atoms may be more common, larger rings do not appear to be ruled out.

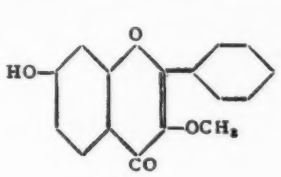
For example, the experiments on the Raman effect of aspirin[4] seem to suggest the existence of chelation involving a ring of 8-atoms as shown below (VIII).



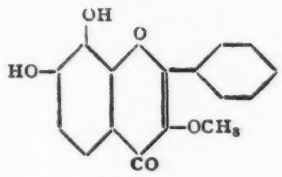
(VIII)

Another point that could be mentioned in connection with the easy isolation of the sulphate described above is the simplicity of the compound and the absence of other solubilising groups. In the case of the 3-methoxy analogue discussed below the sulphate could not be isolated pure though there was evidence of its separation in a small quantity in a colloidal condition.

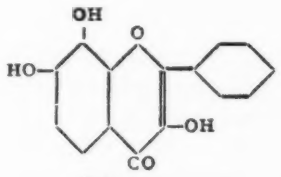
The application of this oxidation to the corresponding flavonols will be useful since it will make the 7 : 8-hydroxy-flavonols more easily available. Otherwise they have to be made by the roundabout method of Kostanecki since ω-methoxy-gallacetophenone has not yet been prepared. 3-Methoxy-7-hydroxy-flavone (IX) which is actually more easy to prepare and which is generally found to be far more reactive in the 8-position than the simpler 7-hydroxy flavone (V) has been subjected to oxidation with persulphate. The yield of the oxidation product is much better (20%) though it is still poor as compared with para oxidations in general. The product (X) has the characteristic properties of a 7 : 8-dihydroxy-compound. On methylation



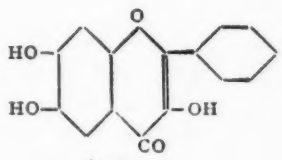
(IX)



(X)



(XI)



(XII)

it gives 3:7:8-trimethoxy-flavone and on demethylation 3:7:8-trihydroxy-flavone (XI). These agree with the description of Dobrzynski and Kostanecki[5] and are different in their properties from isomeric 3:6:7-trimethoxy- and trihydroxy-compounds[6] (XII). Particular mention must be made of lower melting point of 7:8-dihydroxy-flavonol, its deep red colour with alkali and lack of fluorescence in sulphuric acid solution. The 6:7-dihydroxy-flavonol gives only a pale yellow colour with alkali and its solutions have fluorescence. These points are brought out in the following table.

TABLE

	6 : 7-*Dihydroxy-flavonol*	7 : 8-*Dihydroxy-flavonol*
M.P. of Dihydroxy-flavonol ..	318°	249°
,, Triacetyl-derivative ..	191–2°	210–2°
,, Trimethyl-ether ..	175–6°	149–150°
,, 3-Mono-methyl-ether ..	242–4°	220–1°
Colour reactions of the hydroxy-flavonol		
With ferric chloride ..	Dark-greenish brown	Olive brown
,, sodium hydroxide ..	Yellow solution	Red solution
,, concentrated sulphuric acid..	Pale yellow solution with pale blue fluorescence	Yellow solution; no fluorescence
,, sodium carbonate ..	Pale yellow solution	Orange yellow solution
,, alcohol ..	Pale yellow solution; blue fluorescence	Bright yellow solution; no fluorescence

The above experiments show that though oxidation with persulphate does not proceed satisfactorily in the position ortho to an existing phenolic hydroxyl group, it takes place better when the 8-position of flavones is involved. This partly explains why the oxidation of flavones like chrysin with both the hydroxyl groups in the 5- and 7-positions free, takes place more easily than that of the 5-hydroxy compounds. In the former both the para and ortho activating effects exert.

EXPERIMENTAL

7-Hydroxy-flavone required for the oxidations was prepared from resacetophenone benzoate by the method of Baker.[3]

Nuclear Oxidation of 7-hydroxyflavone : preparation of 7:8-Dihydroxy-flavone (VI)

A solution of 7-hydroxy-flavone (2·4 g.) in aqueous alkali (2 g. in 30 c.c. of water) was treated with potassium persulphate solution (4 g. in 60 c.c. of water) during the course of three hours with continuous mechanical stirring, the temperature being kept between 15–20°. The liquid was deep orange red at the end of the addition. It was left overnight, then neutralised

with concentrated hydrochloric acid and the unchanged 7-hydroxy-flavone (1·0 g.) recovered by filtration. The filtrate was extracted twice with ether to remove the last traces of this flavone. Concentrated hydrochloric acid (30 c.c.) was added to the liquid and the mixture heated in the water-bath for 30 minutes. During the course of the hydrolysis, some brownish yellow product separated out. More of it settled down on cooling the mixture to the laboratory temperature. It was filtered, washed with water and crystallised twice from aqueous alcohol when it was obtained as pale yellow stout rhombic prisms melting at 240–42.° Yield 0·3 g. A mixed melting point determination with 7 : 8-dihydroxy-flavone prepared from gallacetophenone benzoate[3] showed no depression. It gave a grass green colour with alcoholic ferric chloride and developed no fluorescence when dissolved in concentrated sulphuric acid or aqueous sodium hydroxide.

The diacetyl derivative was obtained by acetylating the above dihydroxy flavone with acetic anhydride and sodium acetate. It crystallised from aqueous alcohol in the form of colourless needles melting at 198–99°.

7 : 8-Dihydroxy-flavone from the above experiments (0·2 g.) was methylated by refluxing in acetone solution with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (1 g.) for 12 hours. The acetone solution was filtered and the potassium salts washed with hot acetone. The filtrate on evaporation deposited colourless crystals which were recrystallised twice from alcohol. The 7 : 8-dimethoxy-flavone was obtained in the form of thin rectangular rods melting at 151–2°. Its melting point was not depressed when admixed with an authentic sample of 7 : 8-dimethoxy-flavone (Found: C, 71·9; H, 5·3; $C_{17}H_{14}O_4$ requires C, 72·4 and H, 5·0%).

In a repetition of the above experiment after the removal of the unchanged flavone, the neutral reddish brown liquid was treated while cooling under the tap with concentrated hydrochloric acid (30 c.c.). On stirring with a glass-rod, bright shining yellow crystals of the sulphate (VII) separated out in the course of a few minutes. They were collected and thoroughly washed with ether. Yield: 0·3 g. They melted at 225–7° with slight sintering at 220° and appeared as elongated rectangular prisms under the microscope.

To estimate the sulphate in the compound, it was hydrolysed by heating with 1 : 1-hydrochloric acid for 15 minutes in a water-bath and the precipitated flavone filtered off. The sulphate was then precipitated with barium chloride and estimated gravimetrically (Found: SO_4, 28·8; $C_{15}H_{10}O_7S$ requires SO_4, 28·8%).

Nuclear Oxidation of 7-hydroxy-3-methoxyflavone: Preparation of 7:8-dihydroxy-3-methoxyflavone (X)

To a mechanically stirred solution of 7-hydroxy-3-methoxy-flavone (2·4 g.) in aqueous sodium hydroxide (2 g. in 30 c.c.) potassium persulphate (4 g. in 60 c.c. of water) was added dropwise during the course of three hours. The solution was kept at 15–20° throughout the addition. After 24 hours, the solution was neutralised with hydrochloric acid when the unchanged flavone separated out. It was recovered by filtration. The filtrate was extracted twice with ether to remove the last traces. The solution was then rendered strongly acidic by adding concentrated hydrochloric acid (30 c.c.). The liquid which became bright orange-red by this time was heated on the water-bath for about half an hour. There was a gradual separation of a brown solid. On cooling more and more separated out in the form of brown coloured needles. It was filtered, washed with water, and crystallised twice from alcohol when it was obtained as pale yellow rectangular plates melting at 220–21°. Yield, 0·5 g. It gave grass-green colour with ferric chloride in alcoholic solution. There was no fluorescence in concentrated sulphuric acid solution. When its alcoholic solution was treated with magnesium and concentrated hydrochloric acid a bright orange-red colour was developed (Found: C, 59·6; H, 5·1; $C_{16}H_{12}O_5$, $2H_2O$ requires C, 60·0 and H, 5·0%).

The diacetyl-derivative was obtained by refluxing the above flavone with acetic anhydride and dry pyridine for 15 minutes and pouring it into water. It crystallised from ethyl acetate-petroleum ether mixture in the form of micaceous rectangular plates melting at 127–8° (Found: C, 65·5; H, 4·4; $C_{20}H_{16}O_7$ requires C, 65·2 and H, 4·3%).

Methylation of the oxidation product: Preparation of 3:7:8-trimethoxy-flavone

7:8-Dihydroxy-3-methoxy-flavone (0·2 g.) was refluxed in acetone solution with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (2 g.). After 12 hours, the acetone was evaporated and water added to the residue. The methyl ether separated out as a pale yellow solid. It was crystallised from alcohol using a pinch of animal-charcoal. 3:7:8-trimethoxy flavone was obtained in the form of fibrous needles when the crystallisation was rapid. When slowly crystallised aggregates of colourless rectangular prisms were obtained melting at 149–50°. Yield, 0·15 g. (Found: C, 69·3; H, 5·3; $C_{18}H_{16}O_5$ requires C, 69·2; and H, 5·1%).

Demethylation of 7 : 8-*dihydroxy*-3-*methoxy-flavone*: *Preparation of* 3 : 7 : 8-*trihydroxy flavone* (*XI*)

Freshly distilled hydriodic acid (d. 1·7; 17·5 c.c.) was slowly added to the solution of 7 : 8-dihydroxy-3-methoxy-flavone (0·75 g.) in acetic anhydride (10 c.c.) and the solution was refluxed for 1½ hours. It was cooled and water added when a pale yellow precipitate separated out along with some free iodine. Sulphur dioxide was now passed through the mixture till the iodine was completely removed. It was then extracted with ether three times. All the solid went into the ether layer which was finally washed twice with sulphur dioxide water. On removing the ether from the extract by evaporation, a bright yellow crystalline solid was deposited. The compound was crystallised twice from ethyl acetate when the trihydroxy-flavone was obtained as aggregates of rectangular rods melting at 248–9°. Yield, 0·5 g.

It gave a stable red solution in aqueous alkali and an olive brown colour with alcoholic ferric chloride. Its solution in concentrated sulphuric acid was yellow without any fluorescence. It agreed with 7 : 8-dihydroxy-flavonol in all properties as described by Dobrzynski and Kostanecki[5] (Found: C, 66·8; H, 3·6; $C_{15}H_{10}O_5$ requires C, 66·7 and H, 3·7%).

The trihydroxy-flavone was acetylated by refluxing for 20 minutes with acetic anhydride and dry pyridine. The product, obtained on dilution with water, crystallised from alcohol in the form of white needles melting at 210–12°. Dobrzynski and Kostanecki gave the melting point as 210°.

Summary

The possibility of ortho nuclear oxidation in the flavone series has been tested using 7-hydroxy-flavone and 3-methoxy-7-hydroxy-flavone. By means of alkaline persulphate 7 : 8-dihydroxy-flavone (10% yield) and 3-methoxy-7 : 8-dihydroxy-flavone (20% yield) could be obtained. This seems to offer an easier method of preparing the flavonol, 3 : 7 : 8-trihydroxy flavone. The intermediate stage of the sulphate could be isolated pure from 7-hydroxy-flavone.

References

1. Seshadri and co-workers .. *Proc. Ind. Acad. Sci.*, A, 1947, **25**, 417, 427, 432 and 444.
2. Baker, Brown and Scott .. *J. C. S.*, 1939, 1926.
3. Baker .. *Ibid.*, 1933, 1387.
4. Murty and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1944, **19**, 17.
5. Dobrzynski and Kostanecki *Ber.*, 1904, **37**, 2806.
6. Rao, Row and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1945, **22**, 297.

TEMPERATURE VARIATION OF THE REFRACTIVE INDEX OF QUARTZ

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1. Introduction

Accurate determinations of the variation of refractive indices of solids with temperature are of great interest in view of the theory recently developed by G. N. Ramachandran (1946), correlating the variation with the thermal dilatation of the solid on the one hand and with the temperature shift of its electronic spectrum on the other. Such determinations can be carried out by finding the refractive indices of a prism (n) at various temperatures (t) and calculating the rate of change (dn/dt). But there is an easier, and at the same time more accurate way of directly obtaining (dn/dt) by forming interference fringes in a thin plate of the substance and observing the rate of shift of these fringes with temperature. This method, however, requires also an accurate knowledge of the linear expansion of the material in the direction under investigation. For this, the well-known method of Fizeau, again using interferometry, supplies the answer. While most of the data on (dn/dt) for solids have been secured by the use of a prism, there are a few interferometric studies as well, namely, on glasses by Peters, on diamond by Ramachandran and on crystalline quartz by Reimerdes. Prism methods have also been used for quartz.

The application of Ramachandran's theory to these data furnished important conclusions regarding the behaviour of the electronic spectra of solids at different temperatures. In a previous paper appearing in this Journal, the author attempted to apply the theory to crystalline quartz. But he found himself handicapped by the absence of a set of precise values of (dn/dt) over an extensive temperature range (especially low temperatures) and by discrepancies in the data of different workers over restricted temperature ranges. Hence, it was thought desirable to obtain accurate interferometric values of (dn/dt) for the ordinary ray in quartz from the temperature of liquid-air up to 400° C., using the green line of mercury. These measurements were used to calculate the variation of the electronic frequencies of

quartz with temperature. The results have been compared with the cases for a number of other substances.

2. The Experiment

A sample of clear Brazilian quartz was taken and its optic axis determined by immersion in benzene between a pair of polaroids. A thin plate was cut perpendicular to the optic axis, ground and polished. This plate was coated on both sides with a thin film of aluminium by evaporation in vacuum. On placing it normally to parallel monochromatic radiation, a localised transmitted system of fringes was obtained caused by slight local variations in the thickness of the crystal. The aluminising had to be adjusted till this system was quite sharp without undue loss of intensity.

For experiments at high temperatures, the crystal was mounted on a stand specially designed to minimise rotation and buckling. The crystal and part of the stand went into an electrical heater provided with windows for observation and for the introduction of a calibrated thermo-couple kept nearly touching the crystal. For the lower temperatures, the crystal was cemented to a cavity inside a copper block which could be screwed on to a brass tube. This tube slid into an outer tube of glass and the annular space could be kept in continuous evacuation, thereby forming a Dewar flask arrangement. The cooling agents were poured into the brass tube and the temperature could be maintained steady for half an hour.

The optical arrangements were as follows:—A mercury arc was placed immediately behind a circular aperture 2 mm. in diameter. The light from the aperture passed through a green filter and a polariser so oriented that only the ordinary ray would be present in the quartz. On viewing the transmitted light through a microscope focussed on the crystal, the fringes appeared sharply in the field of view. A scratch on the crystal served as a reference mark. On raising the temperature, the fringes appeared to move past the scratch and the temperature corresponding to the transit of each fringe could be noted. By controlling the current, the heating could be made very slow in the neighbourhood of a transit, so that accurate estimates of the temperature and the completion of the transit could be easily obtained. The highest temperature used was 405° C. The readings when the crystal was cooled in the same steps from 405° C. to room temperature and also when the positions of the source and the microscope were interchanged showed no systematic differences, so that the crystal was not tilting or buckling when heated. A series of readings was obtained in this way and the temperatures were plotted against the ordinal numbers of the fringe

shifts. The final transit temperatures were determined from a smooth curve lying evenly between all the points.

For temperatures below that of the room, a different technique had to be adopted since the temperatures could be maintained steady only at certain standard values. Photographs of the fringes were obtained at room temperature, the temperature of carbon dioxide in alcohol (− 98° C.) and the temperature of liquid air (− 188° C.). By putting these photographs under a comparator, fractional fringe shifts past the scratch could be accurately estimated, while the integral parts of the shifts could be estimated visually.

3. Calculation

For normal incidence, any fringe satisfies the relation

$$2n_\omega l = N\lambda, \tag{1}$$

where n_ω is the refractive index and l the thickness of the crystal. Differentiation with respect to the temperature gives

$$2\left(\frac{dn_\omega}{dt}\, l + n_\omega \frac{dl}{dt}\right) \Delta t = \Delta N \cdot \lambda$$

or

$$\frac{dn_\omega}{dt} = \frac{\lambda}{2l}\frac{\Delta N}{\Delta t} - n_\omega \left(\frac{1}{l}\frac{dl}{dt}\right)$$

$$= \frac{\lambda}{2l}\frac{\Delta N}{\Delta t} - n_\omega \alpha, \tag{2}$$

where (α) is the coefficient of linear expansion of the substance along the optic axis.

α was obtained for the mean temperature between two fringe shifts from the formula

$$\alpha = a + 2bt + 3ct^2 + 4dt^3 \tag{3}$$

obtained by differentiation of

$$l = l_0[1 + at + bt^2 + ct^3 + \ldots] \tag{4}$$

The values of the constants are given in the following table:

Table I

Source	Temp. range	$a.\ 10^6$	$b.\ 10^9$	$c.\ 10^{12}$	$d.\ 10^{15}$
Scheel ..	−190° to 100° C.	7·085	9·386	−7·20	0
Lindman ..	9° to 350°	7·159	8·623	+1·87	0
Lindman ..	9° to 434°	7·144	8·925	+0·146	2·75

The coefficients could now be directly calculated from (2), using a value of $n_\omega = 1 \cdot 547$. The values are exhibited graphically in Fig. 1. Table II

TABLE II

Temp. (deg. C.)	$-\frac{dn}{dt}10^6$	Temp. (deg. C.)	$-\frac{dn}{dt}10^6$
−180	4·1	100	6·75
−150	4·4	150	7·40
−100	4·8	200	8·20
− 50	5·2	250	9·20
0	5·65	300	10·50
50	6·15	350	12·95
		380	15·36

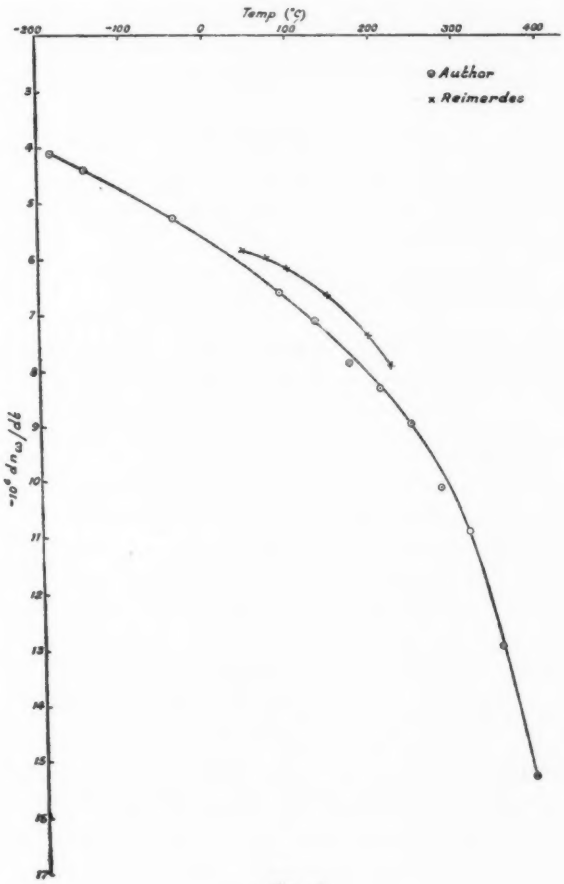

FIG. 1

gives the values for 50° C. intervals read from the graph and Table III the actual refractive indices computed by numerical integration.

TABLE III

Temp. (deg. C.)	Refractive Index	Temp. (deg. C.)	Refractive Index
−188	1·54769	150	1·54583
−100	1·54731	200	1·54544
0	1·54679	250	1·54500
50	1·54650	300	1·54451
100	1·54618	350	1·54394

The only previous work on the 5461 Å line is the interferometric work of Reimerdes from 20° C. to 220°. But his values of the coefficient of linear expansion were too low (Sosman, *The Properties of Silica*, 1927) and hence, his (dn/dt)'s are also too low. Nevertheless, his data have been reproduced in Fig. 1.

4. Discussion

In the previous paper, the author showed that in the case of a substance with a single absorption frequency in the ultra-violet effective in dispersion, a relation of the form

$$\chi_t = p\frac{dn}{dt} + q\gamma_t \tag{1}$$

followed from Ramachandran's theory. Here, (χ_t) is the relative rate of change of electronic frequency with temperature, *i.e.*,

$$\chi_t = \frac{1}{\gamma_t}\frac{d\gamma_t}{dt} = \frac{d(\log \gamma_t)}{dt} \tag{2}$$

(γ_t is the coefficient of cubical expansion of the substance at the temperature (t) and p and q are constants for any particular wave-length. For the λ 5461 line, the formula in the case of quartz becomes

$$\chi_t = 2{\cdot}24\left(\frac{dn_\omega}{dt}\right)_{\lambda 5461} + 1{\cdot}20\gamma_t \tag{3}$$

Using the author's values of $\left(\frac{dn_\omega}{dt}\right)$, χ_t was computed for various temperatures and the dependence on temperature is shown in Fig. 2. The course of the $\chi_t - t$ curve from room temperature to 400° C. is entirely different from what the author calculated in his previous paper, basing himself on Reed's determinations of the temperature coefficient of the extraordinary ndex.

Using Ramachandran's experimental data on (dn/dt) for diamond, and Rinne and Kolb's data on vitreous silica, the author calculated the corresponding values of χ_t for these substances. In the case of zinc-blende, χ_t has been computed by Ramachandran himself. The results are given in Fig. 2. It is evident that the χ values decrease with decreasing temperature, tending to zero as the temperature approaches the absolute zero. In the case of diamond, a substance with a high characteristic temperature, χ_t has

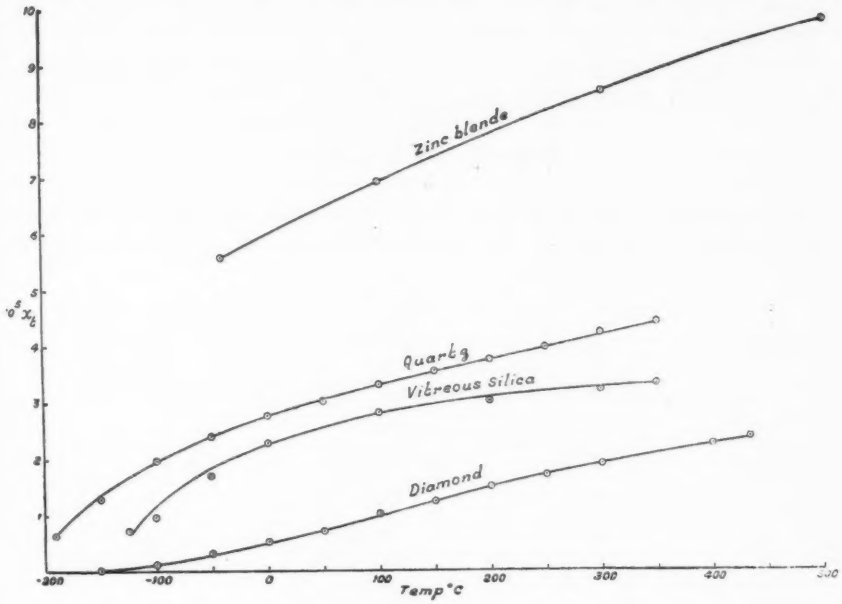

FIG. 2

dropped to zero even at $-$ 150° C. The conclusion is that *as the temperature is lowered, the electronic frequencies of these substances tend to stationary values, their temperature coefficients vanishing.*

The curves for quartz and vitreous silica are seen to be very similar. This is to be expected, owing to the similarity between the two substances, and to the fact that both have absorptions in the same region, namely 1100 Å.U.

In the case of quartz, the value of χ_t near room temperature is $-2{\cdot}8 \times 10^{-5}$. This is the same as the χ_t for the fundamental lattice oscillation at 21 μ (465 cm.$^{-1}$), the temperature shift of which has been measured by Nedungadi (1938). Likewise, the value 350° C. is $-4{\cdot}5 \times 10^{-5}$

which compares with $\chi_t = -4{\cdot}3 \times 10^{-5}$ for the infra-red oscillation. Ramachandran has pointed out that this approximate correspondence holds good in the case of diamond and vitreous silica. At low temperatures, it is well known that the lattice frequencies tend to stationary values. *Thus, the temperature coefficients of the electronic frequencies are of the same order of magnitude as the temperature coefficients of the lattice frequencies.* It would be interesting to obtain (dn/dt) data at low temperatures for many more substances, for instance, the alkali halides, to test the validity of these conclusions for solids in general.

From the values of χ_t, the actual frequency shifts from the value at 0° C. have been calculated according to the formula

$$| \Delta \nu_r |'_0 = \int_0^t \chi_t \, \nu_r \, dt$$

the integration being performed numerically from the graphs. The results are exhibited graphically in Fig. 3. There is a striking resemblance between

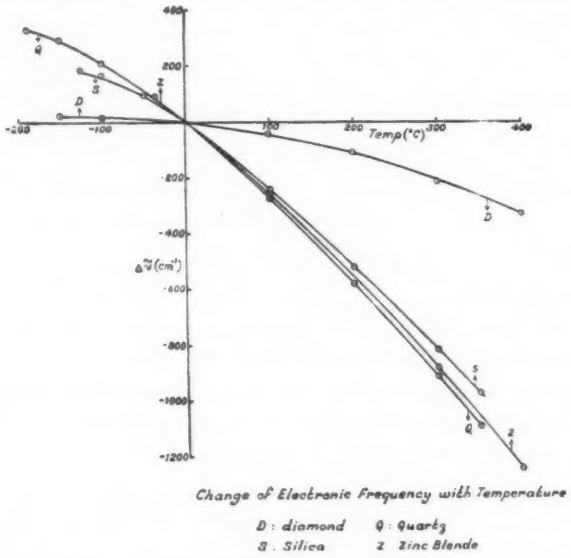

FIG. 3

the curves for zinc-blende, quartz, and vitreous silica, despite the fact that the absorption or zinc-blende is at 2500 Å.U., while the absorptions for quartz and silica are at 1100 Å.U. A low electronic frequency as in zinc-blende corresponds to a weak binding, and hence a large temperature effect,

so that the product is approximately the same as for a crystal with strong binding.

The author expresses here his thanks to Sir C. V. Raman for suggesting this investigation and for guidance during its course.

5. Summary

The temperature coefficient of the ordinary refractive index of quartz for the green line of mercury has been determined from — 190° C. to 400° C., using an interferometric method. The values are used to compute the temperature shift of the electronic frequency in quartz at 1100 Å.U., and the results are compared with those for diamond, zinc-blende, and vitreous silica. It is shown that in the case of diamond, quartz and vitreous silica, the temperature coefficients of the electronic frequencies are of the same order of magnitude as the temperature coefficients of the lattice frequencies. In the case of all the four substances, the electronic frequencies tend to stationary values at low temperatures, so that this result appears to be a general property of solids.

References

1. Sosman, R. B. .. "The Properties of Silica" (American Chemical Society), 1927, Chaps. **20**, 386–87; **34**, 671–97.
2. Micheli, F. J. .. *Arch. Phys. Nat.*, 1902, (4) **13**, 217.
   .. *Ann. d. Physik.*, 1902, (4) **7**, 772.
3. Rinne, F., and Kolb, R. .. *Neues. Jarb. Min.*, 1910, II, 138.
4. Reimerdes, E. .. *Inaug. Dissert. Jena*, 1896, **39**, 14.
5. Ramachandran, G. N. .. *Proc. Ind. Acad. Sci.*, 1946, **25**, 266–375.
6. Radhakrishnan, T. .. *Ibid.*, 1946, **25**, 382.
7. Nedungadi, T. M. K. .. *Ibid.*, 1938, **7**, 86.
8. Reed, J. O. .. *Ann. Physik. V. Chem.*, **1898**, **65**, 707.

THE COLOURING MATTER OF THE TAMARIND SEED TESTA

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Tamarind seed contains nearly 30 per cent. of testa and 70 per cent. of kernel. As a result of the large-scale employment of the kernel flour as a size in the jute and textile industries, vast amounts of the testa are available annually. The testa contains a dyestuff which is used by indigenous dyers for dyeing wool and the shades are said to be all-round fast, comparable with acid and after-chrome dyes.[1] The dyestuff is also regarded suitable for dyeing paper and pulp.[2] The results of a preliminary chemical investigation of this colouring matter are reported in this paper.

The testa can be removed from the seeds by roasting them on hot sand at 125° to 150° for about 20 minutes, and subsequent pounding. It contains 40 per cent. of water-extractable matter of which 80 per cent. is the dyestuff. The latter comprises about 35 per cent. of phlobatannin, 55 per cent. of depside group of tannins and 10 per cent. of an uncharacterized material.

The phlobatannin has been characterized from its response to various reactions characteristic of the group.[3] It undergoes easy acetylation and methylation, yielding almost colourless products.

The depside group of the tanstuff belongs to the catechol class. Its tanning properties are not quite satisfactory, since the leather produced is harsh and highly coloured, and is not considered suitable for shoe uppers. However, in combination with myrobalans, it can be used for tanning heavy hides suitable for sole and suit-case manufacture.

Experimental

Extraction of the testa: isolation of phlobatannin.—The powdered testa (100 g.) was boiled with water (1 l.) for about an hour and a half and filtered through a fine muslin. The residue was similarly extracted 3 times more, in order to complete the extraction. The total extract (about 4 litres) was heated to the boiling point and filtered again. The clear filtrate was made

up to exactly 4 litres, and the total solids in it were estimated, taking an aliquot portion. The rest of the filtrate on standing became opaque and a small amount of a fine solid (No. I) separated as a suspension. After 12 hours the solid was filtered through a fluted filter, since filtration under suction was extremely slow. It was washed with small amounts of cold water, dried first on a steam-bath and then in a vacuum desiccator, and weighed. It was pale brown in colour and was amorphous. It was sparingly soluble in water but readily dissolved in sodium hydroxide or carbonate. In aqueous alcoholic solution it gave a bluish-green colour with ferric chloride. The substance was not further examined.

The clear filtrate after the removal of the above solid was concentrated on a water-bath to about a litre and treated with saturated brine. A flesh coloured precipitate appeared, which was filtered, washed with brine and dried *in vacuo*. The dry solid was powdered and extracted in a soxhlet with alcohol (500 c.c.) which dissolved it almost completely. After concentrating the solution to half its volume, excess of ether was added. The precipitate that separated was further purified by redissolution in alcohol and subsequent reprecipitation with ether. The solid thus obtained (No. II) was filtered, washed with ether and dried in a vacuum desiccator.

All the filtrates and washings from the above (aqueous, alcoholic and ethereal) were mixed together and heated on an electric water-bath to drive off the organic solvents. The aqueous solution was reddish yellow in colour. With ferric chloride it produced a green colour which changed into violet red on the addition of sodium bicarbonate, indicating the presence of compounds with catechol nucleus. It gave tests for the depside group of tannins, which were estimated quantitatively according to the A.O.A.C. Tentative Method of Analysis.[4]

From four sets of experiments conducted with different samples of the testa, the following results were obtained:—

Total solubles: 38–40% of the testa.

Solid No. I: 4–5% of the testa.

Solid No. II: 10–12% of the testa.

Tannins (Depside group): 16–18% of the testa.

Solid No. II was flesh coloured and was amorphous. It was soluble in water, alcohol and acetone, forming reddish solutions, and was insoluble in ether, benzene and chloroform. In sodium hydroxide it dissolved forming deep-red solutions. In 0·5 per cent. solution it responded to all the reactions characteristic of phlobatannins.[3]

Reagent		Result
Alcoholic ferric chloride	..	Dark-green precipitate
Aqueous ferric chloride	..	,, ,,
Gelatine	..	Dirty-white precipitate
Lead acetate	..	Pinkish precipitate soluble in acetic acid
Boiling dilute hydrochloric acid (phlobaphene reaction)		Red precipitate
Bromine water	..	Immediate heavy yellow precipitate
Calcium hydroxide	..	Pinkish colour with a precipitate
Sodium sulphite	..	Light pink colour with a precipitate
Formaldehyde and hydrochloric acid	..	Precipitate on warming
Nitrous acid	..	Immediate brown precipitate
Copper sulphate	..	Faint green precipitate
Copper sulphate and ammonia	..	Heavy brownish-green precipitate
Aqueous ammonia	..	Solution darkens slowly
Potassium dichromate	..	Brown precipitate
Potassium ferricyanide and ammonia	..	Orange-red colour
Hide powder	..	Absorbed
Shavings of sheep skin	..	Tanned

Alternatively the phlobatannin could also be isolated in the form of phlobaphene from the aqueous liquor left after the removal of solid No. I, by the addition of mineral or organic acids in such a quantity as to bring down the pH to between 2·8 and 3·2. In this way, the phlobaphene was obtained as an orange-red precipitate sparingly soluble in water but freely soluble in alkalis.[5]

Acetylation of the phlobatannin.—The purified phlobatannin (5 g.) was treated with acetic anhydride (15 g.) and anhydrous sodium acetate (10 g.), and the mixture was gently boiled under reflux on an oil-bath for 4 hours. It was then cooled and poured over crushed ice and stirred well. The acetyl derivative that separated was filtered, washed and dried. In order to ensure complete acetylation, this product was boiled again for 4 hours with acetic anhydride and anhydrous sodium acetate. The acetate appeared to undergo some decomposition when boiled with hydroxy solvents like alcohol and acetic acid. It was, therefore, purified by dissolving in the minimum amount of acetic anhydride and treating with an equal amount of absolute alcohol, when the substance separated out during the course of a day or two as an almost colourless solid, which exhibited no definite crystalline structure. The yield was 2·5 g. The substance did not melt or decompose below 300° (Found in the sample dried at 110° *in vacuo*: C, 60·0; H, 4·5%). Its optical rotation in glacial acetic acid was determined, since in alcohols and acetone it dissolved sparingly. Even with glacial acetic acid, the solution used to turn brownish red, and so the readings had to be taken in a dilute solution (0·25 per cent. concentration). $\alpha_D^{30°}$ was found to be + 140°.

Methylation of the phlobatannin.—The purified material (5 g.) was dissolved in alcohol (50 c.c.) and treated with dimethyl sulphate (5 c.c.). A 50 per cent. solution of caustic potash (5 c.c.) was added in two instalments with vigorous shaking after each addition. The mixture became hot rapidly and had to be cooled under the tap. When the vigour of the reaction subsided, the process was repeated using the same amount of dimethyl sulphate and alkali. After shaking for about an hour, the mixture was left overnight, filtered and then diluted with an equal amount of water. A pale-brown amorphous solid separated out. To ensure complete methylation the solid was filtered, dissolved in alcohol and treated again with dimethyl sulphate and alkali, as before. The remethylated product was pale brown in colour. For purification it was dissolved in acetone and the solution treated with petroleum ether in drops till it became opalescent. Some coloured impurities were precipitated first and they were removed by filtration. After some time or on the addition of a little more petroleum ether, the methyl phlobatannin separated out as an almost colourless amorphous solid. It gave no colour with ferric chloride in alcoholic solution and did not dissolve in aqueous alkali. It was easily soluble in alcohols, acetone, acetic acid and chloroform, but was sparingly soluble in petroleum ether and benzene. The yield of the pure compound was 1 g. (Found in the sample dried at 110° *in vacuo*: C, 66·3; H, 6·1; OCH_3, 30·6%). Its optical rotation in chloroform solution (0·5 per cent. concentration) was taken and $\alpha_D^{30°}$ was found to be + 130°. On heating it sintered at about 255° and decomposed at 283° to 285°.

Summary

The tamarind seed testa contains about 32 per cent. of tannins of which 35 per cent. is phlobatannin, the rest being mostly catechol tannin. The phlobatannin yields almost colourless methyl and acetyl derivatives which exhibit marked optical activity, supporting the idea that phlobatannins are probably hydroxy flavan derivatives.

References

1. Anon. .. *Jour. Sci. and Ind. Res.*, 1942, **1**, 60.
2. Puntambekar, S. V., and Batra, P. C. .. *Indian Forest Leaflet*, No. 44, 1943.
3. Russel, A. .. *Chem. Rev.*, 1935, **17**, 165.
4. *Official and Tentative Methods of Analysis of the Assn. of Official Agricultural Chemists*, 3rd Ed., 1930, 155.
5. Krishna, S. .. Ind. Patent, 1945, No. 32223.

GRAVITATIONAL METRICS OF SPHERICAL SYMMETRY AND CLASS ONE

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(Communicated by Prof. V. V. Narlikar, F.A.Sc.)

1. Introduction

In general relativity a purely gravitational field is represented by a Riemannian metric of four dimensions. It is sometimes useful to consider the field as immersed in a flat space of higher dimensions. If the lowest number of dimensions of a flat space in which a given Riemannian space of n dimensions can be immersed is $n + p$, the latter is said to be of class p. It is well-known that Schwarzschild's external solution is a Riemannian metric of class two while Einstein's and de Sitter's cosmological models[2] are Riemannian spaces of class one. The present investigation, which was suggested by and carried out under the guidance of Professor V. V. Narlikar, establishes certain class properties for a general spherically symmetrical line-element.

By a suitable transformation of co-ordinates a general spherically symmetrical metric can be reduced to the form,

$$ds^2 = -e^{\lambda}\,dr^2 - r^2\,(d\theta^2 + \sin^2\theta\, d\phi^2) + e^{\nu}\,dt^2, \tag{1}$$

where λ and ν are both functions of r and t. It is obvious that z_1, z_2 and z_3 as given by

$$z_1 = r\sin\theta\cos\phi,\quad z_2 = r\sin\theta\sin\phi,\quad z_3 = r\cos\theta$$

provide

$$dz_1^2 + dz_2^2 + dz_3^2 = dr^2 + r^2\,(d\theta^2 + \sin^2\theta\, d\phi^2). \tag{2}$$

Since a Riemannian space V_n can always be immersed in a flat space of $n(n+1)/2$ dimensions we have for $n = 2$, z_4, z_5, z_6 such that

$$e^{\nu}\,dt^2 - (e^{\lambda} - 1)\,dr^2 = dz_4^2 \pm dz_5^2 \pm dz_6^2. \tag{3}$$

Thus a general spherically symmetrical metric is of class two.

2. Reducibility to Class One

In special cases it may be possible to find real functions z_4 and z_5 such that

$$e^{\nu}\,dt^2 - (e^{\lambda} - 1)\,dr^2 = dz_4^2 \pm dz_5^2,$$

a necessary and sufficient condition[3] for which is that the Gaussian curvature be zero. The condition, when the necessary calculations for (1) are carried out, is found to be

$$e^{\nu}\left(\frac{\nu''}{2}+\frac{\nu'^2}{4}-\frac{\lambda'\nu'}{4}\right)-e^{\lambda}\left(\frac{\ddot{\lambda}}{2}+\frac{\dot{\lambda}^2}{4}-\frac{\dot{\lambda}\dot{\nu}}{4}\right)$$
$$=\tfrac{1}{4}(e^{\lambda}-1)^{-1}(e^{\nu}\lambda'\nu'-e^{\lambda}\dot{\lambda}^2). \tag{4}$$

When and only when (4) is satisfied the metric (1) is of class one.

As explained above the condition (4) really arises out of the V_2 defined by the left-hand side of (3). But it has a significance even in terms of V_4 as given by (1) which has not been, as far as we know, previously stated. It is well-known[4] that when V_4 is of class one, there exists a symmetrical tensor b_{ij} such that

$$R_{hijk}=\pm(b_{hj}\,b_{ik}-b_{ij}\,b_{hk}), \tag{5}$$

the left-hand side being the usual Christoffel Curvature tensor. Calculations show that for (1),

$$\begin{aligned}
R_{1414}&=-e^{\nu}\left(\frac{\nu''}{2}+\frac{\nu'^2}{4}-\frac{\lambda'\nu'}{4}\right)+e^{\lambda}\left(\frac{\ddot{\lambda}}{2}+\frac{\dot{\lambda}^2}{4}-\frac{\dot{\lambda}\dot{\nu}}{4}\right),\\
R_{2323}&=-e^{-\lambda}r^2\sin^2\theta\,(e^{\lambda}-1),\\
R_{3143}&=R_{2142}\sin^2\theta=\tfrac{1}{2}r\sin^2\theta\,\dot{\lambda},\\
R_{1313}&=R_{1212}\sin^2\theta=\tfrac{1}{2}r\sin^2\theta\,\lambda',\\
R_{3434}&=R_{2424}\sin^2\theta=-\tfrac{1}{2}r\sin^2\theta\,e^{\nu-\lambda}\,\nu',
\end{aligned} \tag{6}$$

the remaining 12 of the 20 independent components being identically zero. It is, incidentally, necessary to state here that overhead dashes and dots indicate throughout the paper differentiations with respect to r and t respectively. The variables x^{μ} are defined by

$$x^1=r,\ x^2=\theta,\ x^3=\phi,\ x^4=t.$$

As a result of 12 components being identically zero the only surviving components of b_{ij} are found to be

$$b_{11},\ b_{22},\ b_{33},\ b_{44},\ b_{14}\,(=b_{41}) \tag{7}$$

which, on using (6), gives

$$b_{33}=b_{22}\sin^2\theta. \tag{8}$$

On eliminating the components of b_{ij} from (5) we get

$$R_{1414}\,R_{2323}=R_{1212}\,R_{3434}-R_{2142}\,R_{3143} \tag{9}$$

which is the same as (4), as can be easily verified. If T_μ^ν are the components of the energy-momentum tensor as defined by

$$-8\pi T_\mu^\nu = R_\mu^\nu - \tfrac{1}{2} R g_\mu^\nu \tag{10}$$

the condition* (4) or (9) may be stated as

$$3(1-e^{-\lambda})^2+8\pi r^2(1-e^{-\lambda})(4T_2^2-T_1'-T_4^4)-64\pi^2 r^4(T_1^1T_4^4-T_1^4T_4^1)=0. \tag{11}$$

Let us consider a general spherically symmetrical line-element of the form,

$$ds^2 = -A d\rho^2 - B(d\theta^2+\sin^2\theta\, d\phi^2) + 2c d\rho d\tau + D d\tau^2 \tag{12}$$

where A, B, C and D are all functions of ρ and τ.

The spherical symmetry is preserved for a general transformation,

$$\rho = \bar{\rho}(\rho, \tau),\ \bar{\tau} = \bar{\tau}(\rho, \tau),$$

for which the following can be varified to be invariant:

$$\begin{aligned}&\text{(i)}\ T_1^1+T_4^4,\\ &\text{(ii)}\ T_2^2,\\ &\text{(iii)}\ T_1^1\,T_4^4-T_1^4\,T_4^1,\\ &\text{(iv)}\ B\\ &\text{(v)}\ E \equiv 4B(AD+c^2)\left[D\left(\frac{\partial B}{\partial \rho}\right)^2-2c\frac{\partial B}{\partial \rho}\frac{\partial B}{\partial \tau}-A\left(\frac{\partial B}{\partial \tau}\right)^2\right]^{-1}.\end{aligned} \tag{13}$$

In the case of (1), $E = e^\lambda$ and $B = r^2$. Hence the necessary and sufficient condition (11) may also be expressed as

$$3(E-1)^2+8\pi BE(E-1)[4T_2^2-T_1^1-T_4^4] - 64\pi^2 B^2 E^2 (T_1^1 T_4^4 - T_1^4 T_4^1) = 0, \tag{14}$$

for the general metric (12).

3. Compatible Distributions of Matter

We proceed to investigate perfect fluid distributions of spherical symmetry which are compatible with (1) and (11). For a perfect fluid,

$$T^{\mu\nu} = (p+\rho)\frac{dx^\mu}{ds}\frac{dx^\nu}{ds} - pg^{\mu\nu}, \tag{15}$$

in the usual notation. We now obtain from (11)

$$[3(1-e^{-\lambda})-8\pi\rho r^2][(1-e^{-\lambda})-8\pi p r^2] = 0 \tag{16}$$

---

* The detailed formulæ given by Tolman in *Relativity, Thermodynamics and Cosmology*, 1934, p. 251, are used here.

Two possibilities arise:

$$(a)\ 3(1-e^{-\lambda}) = 8\pi\rho r^2,$$
$$(b)\ (1-e^{-\lambda}) = 8\pi p r^2. \tag{17}$$

In case $\dot{\lambda} = 0$ we have, from the field equations,

$$8\pi T_4^4 = 8\pi\rho = e^{-\lambda}\frac{\lambda'}{r} + \frac{1}{r^2}(1-e^{-\lambda}). \tag{18}$$

From (18) and (17 *a*) we get

$$\rho' = 0 \tag{19}$$

leading to

$$(1-e^{-\lambda})/r^2 = 1/R^2 = 8\pi\rho/3, \tag{20}$$

R being an arbitrary constant. The field equation corresponding to $T_1^1 = T_2^2$ now gives

$$e^{\nu} = [A - B\sqrt{1-r^2/R^2}]^2, \tag{21}$$

where A and B arbitrary functions of time. Thus Schwarzschilds' internal solution is clearly a Riemannian metric of class one. The metric, as given by (20) and (21) for $A = 0$, $B = 1$ and $A = 1$, $B = 0$ is de Sitter's and Einstein's respectively. These cases are inconsistent with the field equations (10) unless they are modified by introducing the cosmological constant. (10) gives

$$\frac{1}{R^2}\cdot\frac{3B(1-r^2/R^2)^{\frac{1}{2}} - A}{A - B(1-r^2/R^2)^{\frac{1}{2}}} = 8\pi p \tag{22}$$

From (18) and (17*b*) we get

$$(\rho - 3p) = p'r \tag{23}$$

which is incompatible with the usual physical conditions,

$$\rho \geqslant 3p \text{ and } p' \leqslant 0 \tag{24}$$

unless

$$\rho = 3p \text{ and } p' = 0 \tag{25}$$

There is no solution of the field equations (10) consistent with (25) unless $p = 0$, $\rho = 0$ in which case the field becomes flat.

When $\dot{\lambda} \neq 0$,

$$8\pi T_4^4 \equiv 8\pi(\rho + p)e^{\nu}\left(\frac{dt}{ds}\right)^2 - 8\pi p = \frac{1}{r^2}(1-e^{-\lambda}) + \frac{e^{-\lambda}\lambda'}{r}. \tag{26}$$

We have also

$$e^{\nu}\left(\frac{dt}{ds}\right)^2 - e^{\lambda}\left(\frac{dr}{ds}\right)^2 = 1. \tag{27}$$

From (26) and (17*a*) we get

$$(p + \rho)\, e^{\lambda} \left(\frac{dr}{ds}\right)^2 = \tfrac{1}{8}\, r\rho', \tag{28}$$

and from (26) and (17*b*)

$$(\rho - 3p) + (\rho + p)\, e^{\lambda} \left(\frac{dr}{ds}\right)^2 = p'r, \tag{29}$$

when use is made of (27). There is no non-trivial solution corresponding to (29).

Summary

It is shown that every gravitational metric of spherical symmetry is in general of class two. A necessary and sufficient condition for the metric to be of class one is obtained in several forms. The limitations imposed by the condition on possible perfect fluid distributions are discussed.

References

1. Eisenhart, L. P. .. *Riemannian Geometry*, 1926, 189.
2. Tolman, R. C. .. *Relativity, Thermodynamics and Cosmology*, 1934, 337–46.
3. Weatherburn, C. E. .. *Riemannian Geometry*, 1942, 117.
4. Eisenhart, L. P. .. *Ibid.*, 197.

STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XXX. Rotatory Dispersion of Camphor Carboxylic Acids, Camphors and 1-Borneol

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In the present communication, we give our determinations of the rotatory dispersion of camphor carboxylic acids in 8 solvents. The influence of the wavelength of light and the nature of the solvent on rotatory power has been briefly discussed. We have also corrected the rotatory dispersion formula of camphor in alcoholic solution, given in an earlier paper.[1] Tables XII and XIII for *l*-borneol are calculated from data given in that paper.

Nature of Rotatory Dispersion

The rotatory dispersion of camphor carboxylic acids in all the solvents is "simple" and can be expressed by the one-term Drude equation, $[\alpha] = \frac{k_0}{\lambda^2 - \lambda_0^2}$. On plotting $1/\alpha$ against λ^2 a straight line is obtained in each case. The dispersion equations have been worked out and the results are given in Tables III to X. It is seen that the differences between the observed specific rotatory powers (*o*) and those calculated from the equation (*c*) agree within the limits of experimental error.

The Effect of the Nature of the Solvent on Rotatory Power

The specific rotatory powers, $[\alpha]^{35°}_{5461}$, of camphor carboxylic acids in eight solvents are given in Table I. The sequence of decreasing rotatory powers is as follows:

Glacial acetic acid > chloroform > water > ethyl alcohol > methyl alcohol > acetone > pyridine > benzene. A comparison of the rotatory powers with the dielectric constants of these solvents [water (80) > methyl alcohol (31·2) > ethyl alcohol (25·8) > acetone (21·5) > pyridine (12·4) > glacial acetic acid (6·4) > chloroform (5·2) > benzene (2·28)] shows that there is a close parallelism between them, only glacial acetic acid and chloroform being anomalous in behaviour. The order of methyl and ethyl alcohols is reversed, but the difference in rotatory power is negligible.

The above order of decreasing rotatory power for the Hg green line (5461 Å.U.) does not hold good for all wavelengths. For mercury violet (4358) it is glacial acetic acid > chloroform > water > methyl alcohol > ethyl alcohol > acetone > pyridine > benzene, the first two not falling in the sequence of decreasing dielectric constants. The order of decreasing

TABLE I

Rotatory Power of Camphor Carboxylic Acid in Different Solvents at 35° C.

Solvent	Dielectric constant	$[\alpha]^{35°}_{5461}$	Absolute Rotation (K_α)
Water ..	78·0	81·50°	19·02
Methyl alcohol ..	31·2	72·50	16·46
Ethyl alcohol ..	25·8	72·58	16·94
Acetone ..	21·5	70·08	16·92
Pyridine ..	12·4	47·58	10·42
Glacial acetic acid ..	6·4	90·58	22·54
Chloroform ..	5·2	85·42	21·15
Benzene ..	2·28	42·00	11·40

TABLE II

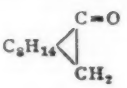
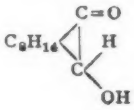
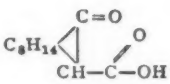
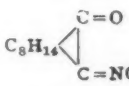
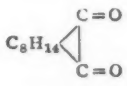
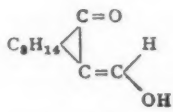
Compound	Structural formula	$[\alpha]^{35°}_{5461}$ in ethyl alcohol
1 Camphor ..		59·61°
2 Borneol ..		43·45
3 Camphorcorboxylic acid ..		72·5
4 Isonitroso camphor ..		241·2 (stable) 214·28 (unstable)
5 Camphorquinone ..		165·54
6 Oxymethylenecamphor ..		243·35

TABLE III

Camphorcarboxylic Acids in Water

$$[\alpha] = \frac{19{\cdot}02}{\lambda^2 - 0{\cdot}0614} \qquad \lambda_0 = 2478 \text{ Å.U.}$$

Dextro Conc. : 0·5000 gm./100 c.c.		Wavelength	$[\alpha]_{cal.}$ (c)	Lævo Conc. : 0·5000 gm./100 c.c.	
$[\alpha]_{obs.}$ (o)	$o-c$			$o'-c$	$[\alpha]_{obs.}$ (o')
48·50°	−0·49°	Li_{6708}	±48·99°	+0·01°	49·00°
..	..	Cd_{6438}	53·92	−0·42	53·50
62·00	+0·81	Li_{6104}	61·19	+0·48	61·67
66·50	−0·12	Na_{5893}	66·62	+0·38	67·00
71·33	+1·52	Hg_{5780}	69·81	+1·36	71·17
81·50	+1·16	Hg_{5461}	80·34	+1·16	81·50
90·67	−0·02	Ag_{5209}	90·69	−0·19	90·50
97·17	+0·70	Cd_{5086}	96·47	+0·37	96·84
114·0	+1·30	Cd_{4800}	112·7	+0·90	113·6
120·5	−0·40	Cd_{4678}	120·9	−0·60	120·3
127·0	+0·40	Li_{4602}	126·6	+0·70	127·3
145·0	−3·00	Hg_{4358}	148·0	+0·50	148·5

TABLE IV

Camphorcarboxylic Acids in Methyl Alcohol

$$[\alpha] = \frac{16{\cdot}46}{\lambda^2 - 0{\cdot}0680} \qquad \lambda_0 = 2608 \text{ Å.U.}$$

Dextro Conc. : 0·5000 gm./100 c.c.		Wavelength	$[\alpha]_{cal.}$ (c)	Lævo Conc. : 0·5000 gm./100 c.c.	
$[\alpha]_{obs.}$ (o)	$o-c$			$o'-c$	$[\alpha]_{obs.}$ (o')
41·67°	−1·41°	Li_{6708}	±43·08°	−0·08°	43·00°
48·00	+0·50	Cd_{6438}	47·50	±0·00	47·50
54·00	−0·05	Li_{6104}	54·05	+0·12	54·17
59·00	+0·05	Na_{5893}	58·95	+0·05	59·00
62·17	−0·67	Hg_{5780}	61·84	±0·00	61·84
72·67	+1·17	Hg_{5461}	71·50	+0·83	72·33
81·00	+0·03	Ag_{5209}	80·97	−0·47	80·50
86·17	−0·13	Cd_{5086}	86·30	+1·03	87·33
102·0	+0·60	Cd_{4800}	101·4	−0·40	101·00
110·3	+1·20	Cd_{4678}	109·1	+0·20	109·30
113·0	−1·50	Li_{4602}	114·5	−0·50	114·0
133·0	−1·90	Hg_{4358}	134·9	+0·10	135·0

TABLE V

Camphorcarboxylic Acids in Ethyl Alcohol

$$[\alpha] = \frac{16{\cdot}94}{\lambda^2 - 0{\cdot}065} \qquad \lambda_0 = 2550 \text{ Å.U.}$$

Dextro Conc. : 0·5000 gm./100 c.c.		Wavelength	$[\alpha]_{cal.}$ (c)	Lævo Conc. : 0·5000 gm./100 c.c.	
$[\alpha]_{obs.}$ (o)	$o-c$			$o'-c$	$[\alpha]_{obs.}$ (o')
43·50°	−0·50°	Li_{6708}	±44·00°	−0·33°	43·67°
49·00	+0·51	Cd_{6438}	48·49	+0·51	49·00
55·00	−0·11	Li_{6104}	55·11	+0·06	55·17
60·00	−0·03	Na_{5893}	60·03	−0·03	60·00
63·00	+0·05	Hg_{5780}	62·95	+0·05	63·00
72·50	−0·14	Hg_{5461}	72·64	+0·03	72·67
82·37	+0·24	Ag_{5209}	82·13	+0·37	82·50
87·33	−0·13	Cd_{5086}	87·46	−0·46	87·00
103·5	+1·10	Cd_{4800}	102·4	−0·40	102·0
110·0	−0·10	Cd_{4678}	110·1	+0·40	110·5
116·7	+1·13	Li_{4603}	115·4	+0·10	115·5
132·5	−3·00	Hg_{4358}	135·5	−0·50	135·0

TABLE VI

Camphorcarboxylic Acids in Acetone

$$[\alpha] = \frac{16{\cdot}92}{\lambda^2 - 0{\cdot}0564} \qquad \lambda_0 = 2375 \text{ Å.U.}$$

Dextro Conc. : 0·5000 gm./100 c.c.		Wavelength	$[\alpha]_{cal.}$ (c)	Lævo Conc. : 0·5008 gm./100 c.c.	
$[\alpha]_{obs.}$ (o)	$o-c$			$o'-c$	$[\alpha]_{obs.}$ (o')
43·00°	+0·02°	Li_{6708}	±42·98°	−0·14°	42·84
48·84	+1·59	Cd_{6438}	47·25	+0·29	47·54
53·50	−0·03	Li_{6104}	53·53	−0·57	52·96
58·84	+0·65	Na_{5893}	58·19	−0·23	57·96
61·00	+0·08	Hg_{5780}	60·92	+0·04	60·96
70·00	+0·02	Hg_{5461}	69·98	+0·18	70·16
79·17	+0·43	Ag_{5209}	78·74	−0·10	78·64
83·00	−0·64	Cd_{5086}	83·64	+0·32	83·96
97·17	−0·08	Cd_{4800}	97·25	−0·45	96·80
104·3	+0·20	Cd_{4678}	104·1	+0·10	104·2
108·5	+0·40	Li_{4603}	108·9	−1·00	107·9
125·0	−1·70	Hg_{4358}	126·7	+0·60	127·3

TABLE VII

Camphorcarboxylic Acids in Pyridine

$$[\alpha] = \frac{10{\cdot}42}{\lambda^2 - 0{\cdot}078} \qquad \lambda_0 = 2793 \text{ Å.U.}$$

Dextro Conc. : 0·5004 gm./100 c.c.		Wavelength	$[\alpha]_{cal.}$ (*c*)	Lævo Conc. : 0·5000 gm./100 c.c.	
$[\alpha]_{obs.}$ (*o*)	*o*−*c*			*o'*−*c*	$[\alpha]_{obs.}$ (*o'*)
28·04°	+0·03°	Li_{6708}	±28·01°	−0·01°	28·00°
30·96	±0·00	Cd_{6438}	30·96	−0·79	30·17
35·32	−0·06	Li_{6104}	35·38	+0·62	36·00
38·94	+0·24	Na_{5893}	38·70	+0·14	38·84
40·48	−0·20	Hg_{5780}	40·68	−0·01	40·67
47·64	+0·32	Hg_{5461}	47·32	+0·18	47·50
53·32	−0·57	Ag_{5209}	53·89	−0·22	53·67
57·16	−0·50	Cd_{5086}	57·66	−1·16	56·50
69·52	+1·15	Cd_{4800}	68·37	−0·04	68·33
73·08	−0·88	Cd_{4678}	73·96	+0·21	74·17
78·16	+0·31	Li_{4603}	77·85	+0·15	78·00
94·32	+1·29	Hg_{4358}	93·03	−0·03	93·00

TABLE VIII

Camphorcarboxylic Acids in Glacial Acetic Acid

$$[\alpha] = \frac{22{\cdot}54}{\lambda^2 - 0{\cdot}0449} \qquad \lambda_0 = 2119 \text{ Å.U.}$$

Dextro Conc. : 0·5000 gm./100 c.c.		Wavelength	$[\alpha]_{cal.}$ (*c*)	Lævo Conc. : 0·5000 gm./100 c.c.	
$[\alpha]_{obs.}$ (*o*)	*o*−*c*			*o'*−*c*	$[\alpha]_{obs.}$ (*o'*)
53·84°	−1·80°	Li_{6708}	±55·64°	−1·47°	54·17°
61·00	+0·01	Cd_{6438}	60·99	+0·34	61·33
67·84	−0·98	Li_{6104}	68·82	−0·82	68·00
75·50	+1·17	Na_{5893}	74·33	+1·34	75·67
78·00	+0·06	Hg_{5780}	77·94	+0·23	78·17
90·84	+1·84	Hg_{5461}	89·00	+1·33	90·33
100·00	+0·44	Ag_{5209}	99·56	+0·61	100·17
105·3	−0·07	Cd_{5086}	105·4	−0·40	105·0
120·5	−1·00	Cd_{4800}	121·5	−0·50	121·0
130·0	+0·40	Cd_{4678}	129·6	−0·10	129·5
135·0	−0·10	Li_{4603}	135·1	+0·40	135·5
158·0	+2·70	Hg_{4358}	155·3	−0·30	155·0

TABLE IX

Camphorcarboxylic Acids in Chloroform

$$[\alpha] = \frac{21{\cdot}15}{\lambda^2 - 0{\cdot}0454} \qquad \lambda_0 = 2031 \text{ Å.U.}$$

Dextro Conc. : 0·5000 gm./100 c.c.		Wavelength	$[\alpha]_{cal.}$ (c)	Lævo Conc. : 0·5000 gm./100 c.c.	
$[\alpha]_{obs.}$ (ρ)	$\rho - c$			$\rho' - c$	$[\alpha]_{obs.}$ (ρ')
+50·50°	−1·78°	Li_{6708}	±52·28°	−1·78°	−50·50°
..	..	Cd_{6438}	57·31	..	..
64·00	−0·68	Li_{6104}	64·68	−1·01	63·67
70·17	+0·09	Na_{5893}	70·08	−0·08	70·00
73·84	+0·60	Hg_{5780}	73·24	+0·60	73·84
85·33	+1·67	Hg_{5461}	83·66	+1·84	85·50
92·50	−1·13	Ag_{5209}	93·63	−0·96	92·67
100·0	+0·62	Cd_{5086}	99·38	+0·46	99·84
114·0	−0·30	Cd_{4800}	114·3	−0·30	114·0
121·5	−0·40	Cd_{4678}	121·9	−0·90	121·0
127·0	−0·10	Li_{4603}	127·1	+0·20	127·3
148·0	+1·80	Hg_{4358}	146·2	+2·80	149·0

TABLE X

Camphorcarboxylic Acids in Benzene

$$[\alpha] = \frac{11{\cdot}40}{\lambda^2 - 0{\cdot}028} \qquad \lambda_0 = 1673 \text{ Å.U.}$$

Dextro Conc. : 4·0000 gm./100 c.c.		Wavelength	$[\alpha]_{cal.}$ (c)	Lævo Conc. : 4·0000 gm./100 c.c.	
$[\alpha]_{obs.}$ (ρ)	$\rho - c$			$\rho' - c$	$[\alpha]_{obs.}$ (ρ')
+27·25°	+0·23°	Li_{6708}	±27·02°	+0·02°	−27·04
..	..	Cd_{6438}	29·49	..	..
33·00	−0·09	Li_{6104}	33·09	+0·16	33·25
35·75	+0·03	Na_{5893}	35·72	−0·12	35·60
37·25	±0·00	Hg_{5780}	37·25	±0·00	37·25
42·00	−0·19	Hg_{5461}	42·19	−0·19	42·00
47·00	+0·14	Ag_{5209}	46·86	+0·14	47·00
49·25	−0·17	Cd_{5086}	49·42	+0·08	49·50
56·50	+0·18	Cd_{4800}	56·32	−0·07	56·25
59·50	−0·23	Cd_{4678}	59·73	+0·02	59·75
62·00	−0·01	Li_{4603}	62·01	−0·01	62·00
70·75	+0·38	Hg_{4358}	70·37	+0·13	70·50

TABLE XI

Camphors in Ethyl Alcohol

$$[\alpha] = \frac{21{\cdot}91}{\lambda^2 - 0{\cdot}087} - \frac{11{\cdot}50}{\lambda^2 - 0{\cdot}037} \qquad \lambda_0 = 2950 \text{ Å.U.} \quad \lambda_0' = 1924 \text{ Å.U.}$$

Dextro Conc. : =33·5415 gm./100 c.c.		Wavelength	$[\alpha]_{cal.}$ (c)	Lævo Conc. : 33·5423 gm./100 c.c.	
$[\alpha]_{obs.}$ (o)	$o-c$			$o'-c$	$[\alpha]_{obs.}$ (o')
+32·52°	±0·00°	Li_{6708}	±32·52°	+0·08°	−32·60
36·41	−0·01	Cd_{6438}	36·42	+0·18	36·60
42·11	−0·34	Li_{6104}	42·45	−0·25	42·20
46·93	−0·20	Na_{5893}	47·13	−0·28	46·85
49·87	−0·07	Hg_{5780}	49·94	−0·08	49·86
59·61	−0·06	Hg_{5461}	59·67	−0·18	59·49
70·10	+0·28	Ag_{5209}	69·82	+0·16	69·98
75·98	+0·24	Cd_{5086}	75·74	+0·36	76·10

TABLE XII

l-Borneol in Benzene

$$[\alpha] = \frac{11{\cdot}80}{\lambda^2 - 0{\cdot}03692} \qquad \lambda_0 = 1921 \text{ Å.U.}$$

Conc. = 6·9010 gm./100 c.c.

Wavelength	$[\alpha]_{cal.}$ (c)	$[\alpha]_{Obs.}$ (o)	$o-c$
Li_{6708} ..	28·56°	−29·34°	+0·78°
Cd_{6438} ..	31·25	31·88	+0·63
Li_{6104} ..	35·18	35·13	−0·05
Na_{5893} ..	38·03	38·11	+0·08
Hg_{5780} ..	39·70	39·70	±0·00
Hg_{5461} ..	45·16	45·21	+0·05
Ag_{5209} ..	50·35	50·28	−0·07
Cd_{5086} ..	..	..	..
Hg_{4358} ..	77·09	77·09	±0·00

rotatory power for Li 6708 is glacial acetic acid > chloroform > water > ethyl alcohol > acetone > methyl alcohol > pyridine > benzene. Here acetic acid, chloroform and methyl alcohol do not follow the sequence of their dielectric constants.

TABLE XIII

l-Borneol in Ethyl Alcohol

$$[\alpha] = \frac{11{\cdot}40}{\lambda^2 - 0{\cdot}03767} \qquad \lambda_0 = 1940 \text{ Å.U.}$$

Conc. = 10·6015 gm./100 c. c.

Wavelength	$[\alpha]_{cal.}$ (*c*)	$[\alpha]_{Obs.}$ (*o*)	*o*−*c*
Li_{6708} ..	27·64°	27·64°	±0·00°
Cd_{6438} ..	30·28	30·25	+0·03
Li_{6104} ..	33·82	34·04	−0·22
Na_{5893} ..	36·42	36·81	−0·39
Hg_{5780} ..	38·25	38·46	−0·21
Hg_{5461} ..	43·45	43·76	−0·31
Ag_{5209} ..	49·24	48·77	+0·47
Cd_{5086} ..	51·71	51·58	+0·13
Hg_{4358} ..	74·90	74·90	±0·00

In view of the contradictory results which are obtained with different wavelengths as in the above discussion, it becomes necessary for a strict comparison that the effects of dispersion should be eliminated. This elimination is easy and fairly accurate in the case of compounds showing "simple" rotatory dispersion. In the Drude equation, if we make $\lambda^2 - \lambda_0^2 = 1$ square micron, the angle of rotation becomes numerically, though not dimensionally, equal to k_0, the 'rotation constant'. This value of specific rotation refers to a wavelength not much greater than 10,000 Å.U., in the infra-red. The longest wavelength for which our observations have been made, Li 6708, is not far removed from this wave-length, and an extrapolation to this value where $\lambda = \sqrt{1 + \lambda_0^2}$ is permissible in view of the linear nature of the dispersion equations. Then the value of the rotation constants may be taken as a measure of the absolute rotatory power of the substances at "corresponding" wavelengths. A comparison may then be made of these constants with the dielectric constants of the solvents.

The values of the absolute rotatory power and the dielectric constant are given in Table I. Only glacial acetic acid and chloroform present anomalous behaviour, whereas the other solvents roughly follow the sequence of their dielectric constants.

CASE OF GLACIAL ACETIC ACID

The anomalous behaviour of camphor carboxylic acid in glacial acetic acid may be explained in the following way: It was found in an earlier investigation[2] that the specific rotation of camphor carboxylic acid in water

increases with concentration. On the electrolytic dissociation hypothesis, the acid at higher concentrations is less dissociated. If the undissociated acid molecule has a higher specific rotation than the acid ion, the specific rotation would rise with concentration. On the basis of this assumption, the increase in specific rotation of camphor carboxylic acid in water at higher concentrations is explained. In an acid medium, the rotation should be higher due to the suppression of ionisation. Camphor carboxylic acid in glacial acetic acid solution shows the highest rotatory power of all the solvents, in conformity with the above assumption.

Physical Identity of Enantiomers

The rotatory powers of *d*- and *l*-forms of camphor carboxylic acid are identical in all the solvents examined, and this lends further support to Pasteur's Principle of Molecular Dissymmetry. Out of 187 observations recorded in this paper, in as many as 151 cases, the difference in the numerical values of the specific rotatory power of the optically active and opposite isomers corresponds to an angle of less than 0·01° in the observed angle of rotation and in 30 cases the corresponding angle lies between 0·01° and 0·02° which is within the limits of experimental error allowed in these measurements. In the remaining six cases this difference corresponds to about 0·03°, mostly for Hg violet line which is difficult to read. All these differences are, however, of the nature of casual experimental errors.

Rotatory Dispersion Equations for Camphors and *l*-Borneol

The rotatory dispersion of Camphors in alcoholic solution (conc. 33·5415 gm./100 c.c.) has been recorded by Singh and Mahanti in an earlier paper.[1] The dispersion formula is, however, wrongly recorded. We have re-calculated the two-term Drude equation and find it to be

$$[\alpha] = \frac{21 \cdot 91}{\lambda^2 - 0 \cdot 087} - \frac{11 \cdot 50}{\lambda^2 - 0 \cdot 037}$$

This gives 2 values for the dominant absorption bands at λ 1924 Å.U. and λ 2950 Å.U. One of these at λ 1924 Å.U. has been identified with λ 1912 Å.U. derived from refractive dispersion equation[3] and the other at λ 2950 Å.U. corresponds to λ 2874 Å.U. and λ 2890 Å.U. determined from direct absorption measurements by Baly *et al.*[4] and Hartley[5] respectively.

The differences between the calculated and observed values of rotatory power of the *d*- and *l*-camphors are shown in Table XI.

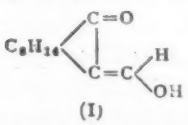
In the same paper by Singh and Mahanti the rotatory dispersion of *l*-Borneol in benzene and ethyl alcohol has been recorded, but no dispersion equations had been worked out. We have now calculated the one-term

Drude equations which fit the data (Tables XII and XIII). The value of λ_0 the dominant absorption band in alcohol (λ 1940 Å.U.) deduced from the rotatory dispersion equation agrees with that obtained from refractive dispersion data (λ 1962 Å.U.).

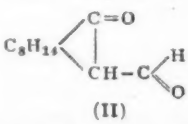
Chemical Constitution and Optical Rotatory Power

The effect of the structure of a molecule on rotatory power is well illustrated by comparing the specific rotation $[\alpha]^{25°}_{5461}$ of the six compounds camphor, borneol, camphor carboxylic acid, iso-nitroso camphor (stable and unstable), camphorquinone and oxymethylenecamphor (Table II). The replacement of a hydrogen atom of the methylene group of camphor (1) by an $-OH$ group in borneol (2) lowers rotation from 59·6° to 43·45°. In camphor-quinone the methylene group is converted to a keto group producing an ortho diketone in which the two $-C=O$ groups are in complete conjugation. This has raised the rotation to a much higher value (165·5°). The introduction of the oximino group $=N-OH$ for the two atoms of hydrogen in the methylene group of the camphor molecule as in iso-nitroso camphors, (4) has also brought about a complete conjugation between the keto and the $=N-OH$ groups, accompanied by a still larger rise in rotatory power from 59·6° to 241·2° (stable) and to 214·8° (unstable). In the case of camphor carboxylic acid, the conjugation of the keto group with the $-C\langle^{O}_{OH}$ group is however broken by two consecutive single bonds, thus $\langle^{C=O}_{CH-C=O}$ (OH). The resulting increase in rotation is accordingly small (59·6° to 72·5°).

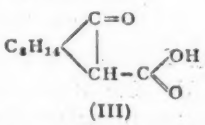
Oxymethylene camphor has been represented by formula I



(I)



(II)



(III)

The aldehydic formula II is very similar to that of camphor carboxylic acid III, the only difference being the replacement of $-OH$ group by a hydrogen atom. On this formulation and on the above-mentioned analogy and comparison of the rotatory power of borneol and camphor, where the replacement of one hydrogen atom for one hydroxy group raises the rotation by about 16°, the value of rotatory power of oxymethylene camphor should be only slightly higher for formula II than that of camphor carboxylic acid, namely 72·5°. But the observed rotatory power of oxymethylene camphor[6]

is the highest of all the compounds given in Table II, namely, 243·35°. This strongly supports formula I for oxymethylene camphor as this shows a complete conjugation between the keto and the ethylenic bonds which is however not the case with formula II. This is in harmony with previous work by one of us[7] in which oxymethylene camphor was given formula I, but in solution was found to undergo mutarotation with an equilibrium value of ± 229·5° between the two modifications I and II.

Experimental

Camphorcarboxylic acids, *d*-, *l*-, and *dl*-, were prepared and purified by the method of Bredt.[8]

The rotatory power determinations were carried out in a 2-dcm. jacketed tube at 35° C. The values of the λ_0 calculated from the dispersion formulæ are given in the tables and stated in Å.U.

Summary

1. The rotatory dispersion of *d*- and *l*-camphorcarboxylic acids in 8 solvents is described. The dispersion is simple and obeys the one-term Drude equation.

2. The effect of solvents on the rotatory power is discussed.

3. The effect of constitution on rotatory power of camphorcarboxylic acid is also discussed.

4. The *d*- and *l*-forms give identical rotation within the limits of experimental error and thus support Pasteur's Law of Molecular Dissymmetry.

5. The formula for the complex dispersion of *d*- and *l*-camphors in ethyl alcohol has been recalculated. The simple rotatory dispersion formulæ for *l*-borneol in ethyl alcohol and benzene have also been calculated.

We wish to make grateful acknowledgements to the University of Allahabad for providing research facilities and for the award of the Empress Victoria Readership to one of us (B. K. K. N.).

References

1. Singh, B. K., and Mahanti, I. *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 378.
2. ——— and Nayar, B. K. K. *Ibid.*, 1947, **26**, 271.
3. ——————— .. *Ibid.*, 1947, **26**, 261.
4. Baly, Marsden and Stewart *J. C. S.*, 1906, **89**, 979.
5. Hartley .. *Ibid.*, 1908, **93**, 961.
6. Singh, B. K., and Bhaduri, B. *J. C. S.*, 1930, **7**, 771.
7. ——— and Srinivasan, M. K. *Proc. Ind. Acad. Sci.*, A, 1940, **12**, 21.
8. Bredt .. *Ber.*, 1891, **24**, 3382.

PRODUCTION OF *JOSHI-EFFECT* IN AIR UNDER ELECTRICAL DISCHARGE: THE RÔLE OF SORBED CHLORINE

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The discovery of the *Joshi-Effect* Δi[1-6, 10], an instantaneous and reversible photo-diminution of the current i, opens a new field in studies of photo-reactions at gas-solid interface under electrical excitation.[11] Earlier results of Joshi and co-workers on certain hysteresis effects in bromine[3] and chlorine,[7] the time-variation of Δi in a number of gases,[2,8,12,27] the marked influence of traces of impurities and the 'wall-effect' in electrically excited systems[3,9,15,16] have revealed that the nature of the electrode surface[12, 13, 14] represents an important determinant of this new phenomenon. It was of interest, therefore, to investigate the possible contribution of sorbed chlorine in the observed *Joshi-Effect*.

§1. The general arrangement of the apparatus is shown in Fig. 1. It consisted essentially of a Siemens' type (glass) ozoniser excited by a transformer discharge of 500 cycles frequency in the primary supply. The system was irradiated, transversely to the ozoniser axis, by operating a Shutter (Fig. 1) between it and a 100 watt incandescent (glass) bulb run at 180 volts. The ozoniser was filled with the gas at the desired pressure (p. mm. Hg.). The discharge current was measured *simultaneously* with a double-wave, metal oxide, rectifier and a vacuo-junction introduced serially in the low tension circuit; separate galvanometers were used. The galvanometer deflections using the oxide rectifier indicate the corresponding current i, those with the vacuo-junction are a measure of i^2. The discharge current i_1D and i_2D, using the above two detectors respectively at an applied potential [kV, kilo-volts (r.m.s.)] was first measured in dark and when the ozoniser was exposed to light. The difference Δi_1 and Δi_2 is a measure of the *Joshi-Effect*; the corresponding relative values, which are more convenient for purposes of comparison of the *effect* under various conditions, $\frac{\Delta i_1}{i_1 \mathrm{D}} \times 100$ and $\frac{\Delta i_2}{i_2 \mathrm{D}} \times 100$, using the oxide rectifier and the vacuo-junction respectively are denoted by $\% \Delta i_1$, and $\% \Delta i_2$.

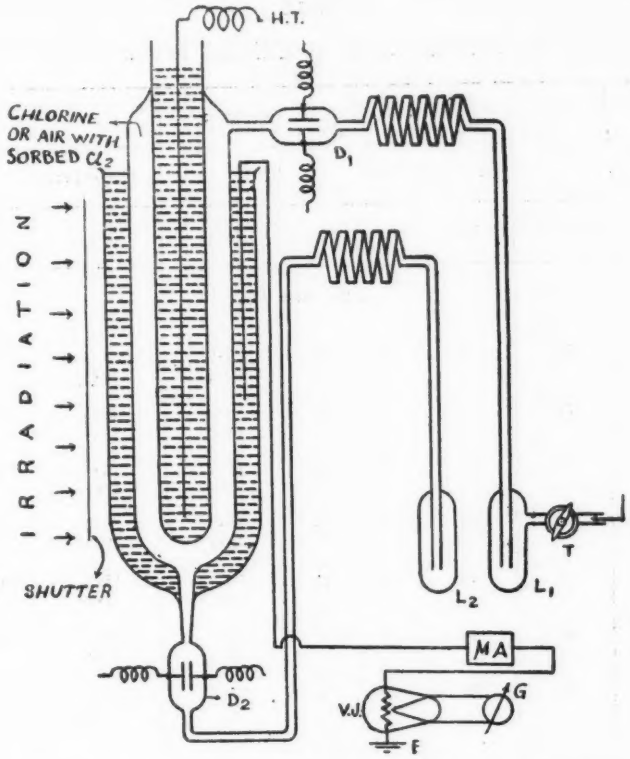

FIG. Influence of Chlorine Sorbed under Electrical Discharge on *Joshi-Effect* in Air

§2. The ozoniser was first filled with a mixture of purified air and chlorine (containing about 75% Cl_2) at pressures 215 and 260 mm. Hg.; these were found to be optimum in respect of Δi as shown by results of a number of trial experiments. After observing the *effect* Δi at applied potentials varied in the range 1–3 kV at the above pressures (Table I), the ozoniser was evacuated on the topler but not degassed (*vide infra*). It was then filled with purified and well-dried air at the above pressures and the corresponding results for Δi recorded. It was remarkable to see that the magnitude of Δi in (this sample of) air was almost equal to that in the above chlorine-air mixture (Tables I and II). During this stage of the work, it was observed that compared with the results in chlorine and chlorine-air mixture, the influence of '*aging*' on Δi in all the samples of air (with residual sorbed chlorine) deviated markedly (Table II).

TABLE I

Joshi-Effect *in Air-Chlorine Mixture*

Applied potential kV (r.m.s.)	Detector							
	Metal oxide rectifier				Vacuo-junction			
	Dark	Light	Δi	$\%\Delta i$	Dark	Light	Δi	$\%\Delta i$
				p : 215 mm. Hg.				
1·53	15	8	7	47	7·0 (2·6)	4·5 (2·1)	0·5	20
1·60	20	13	7	35	8·0 (2·8)	4·3 (2·1)	0·7	16
1·73	30	23	7	23	10·7 (3·3)	7·0 (2·7)	0·6	9
1·86	40	34	6	15	13·3 (3·7)	9·0 (3·0)	0·7	8
2·00	52	46	6	12	16·5 (4·1)	11·5 (3·4)	0·7	6
2·13	64	58	6	9	19·5 (4·4)	13·0 (3·7)	0·7	5
2·27	72	66	6	8	22·0 (4·7)	15·5 (3·9)	0·8	5
				p : 260 mm. Hg.				
1·60	10	1	9	90	4·5 (2·1)	3·0 (1·7)	0·4	20
1·73	21	13	8	40	6·8 (2·6)	4·5 (2·1)	0·5	20
1·86	30	22	8	27	8·8 (3·0)	6·0 (2·5)	0·5	17
2·00	41	34	7	18	11·0 (3·3)	7·5 (2·7)	0·6	18
2·07	51	44	7	14	13·0 (3·6)	9·0 (3·0)	0·6	16
2·13	60	53	7	11	15·0 (3·9)	10·7 (3·3)	0·6	16
2·27	71	64	7	10	17·4 (4·2)	12·7 (3·5)	0·7	17

TABLE II

Joshi-Effect *in Air*: *Influence of a Progressive Decrease of Sorbed Chlorine*

(The ozoniser was charged with air at a constant pressure, subjected to discharge, the corresponding Δi observed, and toplered out on successive days, *a*, *b*, *c*, ... *f*.)

Applied potential kV (r.m.s.)	Detector							
	Metal oxide rectifier				Vacuo-junction			
	Dark	Light	Δi	$\%\Delta i$	Dark	Light	Δi	$\%\Delta i$
0·8	1	−5	6	..	2·1 (1·5)	1·1 (1·1)	0·4	24
0·93	8	0	8	100	3·8 (2·0)	2·4 (1·6)	0·4	20
1·06	12	4	8	67	4·3 (2·2)	3·4 (1·8)	0·4	18
1·20	20	12	8	40	6·6 (2·6)	4·6 (2·2)	0·4	15
1·33	27	20	7	25	7·9 (2·8)	5·8 (2·4)	0·4	14
1·47	36	30	6	17	9·6 (3·1)	7·5 (2·7)	0·4	13
1·60	48	43	5	10	12·0 (3·5)	9·6 (3·1)	0·4	11
1·73	55	51	4	7	13·2 (3·6)	11·1 (3·3)	0·3	8
1·87	68	65	3	4	15·7 (4·0)	13·6 (3·7)	0·3	8
				(*a*)				
0·8	−1	−4	3	..	1·4 (1·2)	1·0 (1·0)	0·2	17
0·93	6	2	4	67	3·5 (1·9)	2·9 (1·7)	0·2	10
1·06	11	7	4	36	4·8 (2·2)	4·0 (2·0)	0·2	9
1·20	16	12	4	25	5·8 (2·4)	4·8 (2·2)	0·2	8
1·33	21	18	3	14	7·5 (2·7)	6·3 (2·5)	0·2	7
1·47	32	30	2	6	9·0 (3·0)	7·7 (2·8)	0·2	6
1·60	43	40	3	7	11·0 (3·3)	9·5 (3·1)	0·2	6

TABLE II—(*Contd.*)

Applied potential kV (r.m.s.)	Detector							
	Metal oxide rectifier				Vacuo-junction			
	Dark	Light	Δi	$\%\Delta i$	Dark	Light	Δi	$\%\Delta i$
1·73	55	53	2	4	13·2 (3·6)	11·8 (3·4)	0·2	6
1·87	68	66	2	3	16·0 (4·0)	14·5 (3·8)	0·2	5
				(*b*)				
0·8	−1	−4	3	..	1·0 (1·0)	0·8 (0·9)	0·1	10
0·93	5	1	4	80	1·2 (1·1)	0·9 (0·95)	0·15	14
1·06	10	7	3	30	2·6 (1·6)	2·2 (1·5)	0·1	6
1·20	15	12	3	20	3·0 (1·7)	2·6 (1·6)	,,	6
1·33	23	21	2	9	4·0 (2·0)	3·5 (1·9)	,,	5
1·47	30	28	2	6	5·4 (2·3)	4·8 (2·2)	,,	4
1·60	39	37	2	5	6·7 (2·6)	6·2 (2·5)	,,	4
1·73	52	50	2	4	9·0 (3·0)	8·2 (2·9)	,,	3
1·87	62	61	1	2	10·3 (3·2)	9·7 (3·1)	,,	3
				(*c*)				
0·80	−1	−4	3	..	1·2 (1·1)	1·0 (1·0)	0·1	9
0·93	3	1	2	67	2·7 (1·6)	2·4 (1·5)	,,	6
1·06	10	8	2	20	4·0 (2·0)	3·6 (1·9)	,,	5
1·20	17	15	2	12	5·5 (2·3)	5·0 (2·2)	,,	4
1·33	27	25	2	7	7·0 (2·6)	6·4 (2·5)	,,	4
1·47	35	33	2	6	8·2 (2·9)	7·6 (2·8)	,,	3
1·60	47	46	1	2	10·2 (3·2)	9·6 (3·1)	,,	3
1·73	58	57	1	2	12·0 (3·5)	11·0 (3·3)	0·2	6
1·87	68	67	1	2	13·0 (3·6)	12·2 (3·5)	0·1	3

TABLE II—(*Contd.*)

Applied potential kV (r.m.s.)	Detector							
	Metal oxide rectifier				Vacuo-junction			
	Dark	Light	Δi	$\%\Delta i$	Dark	Light	Δi	$\%\Delta i$
				(*d*)				
0·8	−2	−4	2	..	0·7 (0·8)	0·5 (0·7)	0·1	13
0·93	4	1	3	75	2·1 (1·5)	1·7 (1·3)	0·2	13
1·06	9	7	2	22	3·0 (1·7)	2·6 (1·6)	0·1	6
1·33	25	23	2	8	5·2 (2·3)	4·7 (2·2)	,,	4
1·47	36	34	2	6	6·4 (2·5)	5·9 (2·4)	,,	4
1·60	47	46	1	2	7·7 (2·8)	7·2 (2·7)	,,	4
1·73	57	56	1	2	9·0 (3·0)	8·5 (2·9)	,,	3
				(*e*)				
1·06	12	10	2	17	4·3 (2·1)	3·8 (2·0)	0·1	5
1·20	20	18	2	10	5·4 (2·3)	4·9 (2·2)	,,	4
1·33	28	26	2	8	6·6 (2·6)	6·0 (2·5)	,,	4
1·47	39	38	1	3	8·3 (2·9)	7·7 (2·8)	,,	3
1·60	48	47	1	2	9·7 (3·1)	9·0 (3·0)	,,	3
				(*f*)				
1·06	14	12	2	14	3·8 (1·9)	3·3 (1·8)	0·1	5
1·20	21	19	2	10	4·9 (2·2)	4·4 (2·1)	,,	5
1·33	31	29	2	6	6·0 (2·5)	5·4 (2·3)	0·2	8
1·47	40	39	1	3	7·2 (2·7)	6·7 (2·6)	0·1	4
1·60	53	52	1	2	8·7 (2·9)	8·1 (2·8)	,,	3
1·73	65	64	1	2	10·4 (3·2)	9·8 (3·1)	,,	3

§3. The influence of sorbed chlorine on the *effect* Δi was further investigated as follows:

Pure and well dried chlorine was introduced in the ozoniser at pressures which were increased progressingly upto the atmospheric and the system allowed to stand over for periods varied in the range of one to seven days. After this, the ozoniser was exhausted on the topler and filled with dry air at various pressures. Results of experiments carried out as in §2 show that the *Joshi-Effect* Δi, was negligibly small. This shows that sorption of neutral chlorine on the annular walls of the unexcited ozoniser does not contribute to the production of the *Joshi-Effect*.

In the second series of experiments, the ozoniser was connected between two sets of Crookes type discharge tubes, D_1 and D_2, which in turn were connected to two traps L_1 and L_2 (Fig. 1) cooled by liquid air, through long capillary leaks which served to regulate the transpiration pressure of the gas admitted from L_1 to L_2 and *vice versa*. The entire assembly of apparatus was first evacuated on the topler. A considerable quantity of chlorine, purified by fractionation over liquid air, was collected in L_1; the tap T was then closed. The trap L_2 was immersed in liquid air and chlorine was allowed to evaporate in L_1 by removing the liquid air. The Crookes tube D_1 was then excited with a H.T. transformer. D_1 and D_2 were connected to the ozoniser by about 4 cm. medium bore tubes. This short length, and the pressure gradient between L_1 and the ozoniser, and L_2 and the ozoniser in the reverse operation, ensured that, at any rate, a part of the chlorine admitted to the ozoniser was activated by the discharge. When the whole gas was collected in L_2, the trap L_1 was cooled by liquid air and chlorine was allowed to evaporate from L_2. This time the streaming gas was subjected to a discharge in D_2. This operation was repeated for about 12 hours. Finally, the chlorine was toplered out of the entire apparatus. As described in §2, air at various pressures was introduced in the ozoniser. It was observed that even at the optimum pressure, Δi was but negligibly small with the available detectors. This shows that sorption of presumably atomised chlorine on the glass walls, *per se*, is not a sufficient condition for the production of Δi.

§4. The ozoniser was next filled with chlorine at about 300 mm. Hg. and was subjected *intermittently* to a discharge for about 14 hours. After toplering out the chlorine, pure and dry air was once again admitted as in §2. The system now showed a pronounced *Joshi-Effect*, Δi, corresponding to 88% photo-diminution of the current; and what appeared significant was a marked and progressive decrease in Δi on '*aging*' the system under discharge, at different applied potentials (Table III, Fig. 3). These results

TABLE III

Variation of Joshi-Effect *in air due to desorption of chlorine on* '*aging*' *at different applied potentials*

Time (minutes)	Applied potential kV (r.m.s.)	Dark	Light	Δi	$\% \Delta i$
..	0·67	8	1	7	88
0·5	1·06	30	23	7	23
1·0	,,	,,	25	5	17
1·5	,,	,,	25	5	17
2·0	,,	,,	25	5	17
2·5	1·20	37	35	2	5
3·0	1·33	48	47	1	2
3·5	,,	,,	,,	,,	,,
4·0	,,	,,	,,	,,	,,
4·5	,,	,,	,,	,,	,,
5·0	,,	,,	,,	,,	,,

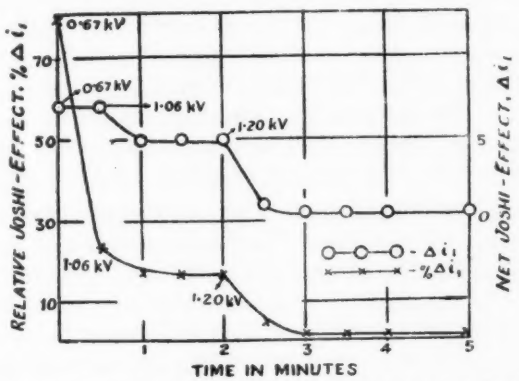

FIG. 3. Variation with Aging of *Joshi-Effect* in Air with Sorbed Cl_2

also show that whilst an increase in the applied potential from 0·7 to 1·1 kV (r.m.s.) i_1D increased from 8 to 30 micro-amps, Δi_1 remained practically the same, *viz.*, 7 micro-amps. The corresponding relative *Joshi-Effect*, however, decreased from 88 to 23. On '*aging*' under the discharge at the higher potential, $\% \Delta i_1$ decreased further to, and remained stationary at 17.

It is instructive at this stage to consider a general theory due to Joshi,[14, 20] for the *effect* Δi. He assumes an adsorption-like electrode layer as the chief seat of this phenomenon. Irradiation releases electrons from this layer as determined by its characteristic 'work-function'. These are captured to form negative ions such as Cl^-, Cl_3^- due to the high electron affinity of chlorine which is atomised and excited in the discharge. These slow moving ions formed near the electrode reduce the current to give Δi, as a space-

charge effect. The following equation for the conductivity in an ozoniser type discharge, which is well adapted for the production of Δi is due to Joshi.[20]

$$i = \frac{V}{jL\,\Sigma f + \frac{1}{jC_w\,\Sigma f} + \frac{1}{\frac{1}{R_g} + jC_g\,\Sigma f}}$$

where Σf represents not only the frequency of the A.C. supply and its harmonics, but also of those produced under the discharge;

C_w is the combined capacity due to the inner and outer electrodes of the ozoniser;

C_g is the capacity of the annular space filled with the gas;

and R_g is the inverse of conductivity produced in the gas as a result of ionization at the applied potential V.

The results in Table III for the *Joshi-Effect* in air with sorbed chlorine show that the current in dark, i_1D is not effected sensibly under '*aging*' at a given potential. It follows, therefore, from (1) that C_w, C_g and R_g are not altered due to '*aging*'; this last reduces, however, to a marked extent the *effect* Δi_1. This may be therefore attributed to an alteration (increase) of the 'work-function', which is a chief determinant of Δi in Joshi's theory.

The formation of the adsorption layer contemplated in the above theory is not (necessarily) instantaneous; its break up during '*aging*' may well therefore be a time process, and is attributable to the removal of chlorine as a result of ionic bombardment. This removal is expected to be greater when the sorbed layer is in contact with excited air, than with pure chlorine and air-chlorine mixtures rich in the latter. This explains the rapid diminution of $\%\ \Delta i_1$ (Table III) during about 5 minutes of exposure to discharge. It may be mentioned at this stage that in an experiment which was typical of a series, when first the ozoniser was subjected to discharge in pure chlorine for a period shorter than that mentioned above, and the chlorine was toplered out and replaced by air as in §2, a *Joshi-Effect* as large as 90% was observed which, however, diminished rapidly to a negligibly small value within but two minutes of exposure to discharge.

Manley[23] found a glow discharge capable of freeing glass surfaces from residual gases or vapours, which could not be removed by mere evacuation. Desorption of numerous gases was also effected similarly by Pirain.[24]

§5. The results of a number of workers[21, 22] in these Laboratories have shown that under a fairly wide range of representative conditions, the magnitude of the *Joshi-Effect*, Δi in air is low compared with that in the halogens,

oxygen, etc. This follows from Joshi's theory of the *effect*, Δi in which the electron affinity of the excited medium plays an important role.[10, 12, 14, 20] Joshi's general result that the normally low Δi, characteristic of air, is enhanced by admixture with but small proportion of chlorine, bromine, and iodine, roughly in the order of their electron affinities, receives a ready explanation[20]; as also the author's finding that with a fixed mass of air and constant exciting conditions, Δi diminishes as the proportion of admixed chlorine is reduced progressively. In the present work, the system being exhausted on the topler, the pressure of a gas, *e.g.*, like residual chlorine, can be only a small fraction of mm. Hg. This (partial) pressure of chlorine is insufficient to produce a detectable Δi in air. It is remarkable, therefore, to observe the large magnitude of *Joshi-Effect* in air when the ozoniser was pretreated with chlorine (under electrical discharge) (Fig. 3, §3). This may be attributed to the sorption of chlorine, which had taken place when the system was subjected to electrical discharge with pure chlorine and chlorine-air mixture (Tables I and III). During a detailed investigation in these Laboratories, Shanmukharao[16] found HCl, in the pressure range 10–300 mm. Hg., showed a large Δi and that when the HCl was replaced by air as in §2, an *effect* about as large as that with HCl was observed. This was traced by Joshi to the presence of sorbed HCl. The influence of '*aging*', of the applied potential and especially the reduction of Δi, when the ozoniser was washed with successive samples of air are explicable on the hypothesis that the sorbed HCl, along with the chlorine formed by its dissociation, provided the main seat of Δi. That the *effect*, Δi, was not observed, under a wide range of conditions, sensibly identical with those mentioned above, when the ozoniser surface was allowed to have prolonged contact with ordinary chlorine and that preactivated by electrical discharge (§3) suggests the following: The sorption of chlorine, produced under electrical fields intense enough to cause ionization by collision is different from and possibly greater than that with ordinary chlorine, and that preactivated partially. It is suggested that it is the former sorption, *i.e.*, under electrical fields, which contributes to the production of *Joshi-Effect* as shown by results in Tables II and III.

The concentration of sorbed chlorine would be equilibrium with that in the homogeneous gas phase, *i.e.*, air, excited under discharge. Part of the chlorine is then removed when the air is toplered out (§2) resulting in a lowered Δi in the next experiment (Table II). The chlorine was completely removed as the ozoniser was thus fed successively with different charges of air; finally, the *Joshi-Effect* became negligibly small corresponding to the complete desorption of Cl_2 (Fig. 2, Table II). Results given in Table III, however, show that this influence on Δi in air of 'sorbed' chlorine is but

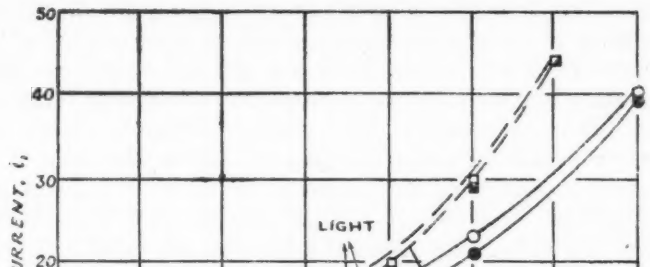

FIG. 2. Comparative *Joshi-Effect* in Chlorine and in Air with Sorbed Chlorine

short-lived. Besides, whilst in general, '*aging*' in chlorine or Cl_2-air mixture was found to bring about an increase in Δi,[8] its effect on air (in these experiments, *i.e.*, in the presence of sorbed Cl_2) was just in the opposite direction; a considerable decrease in Δi was noticed (Table III).

§6. The possible dependence of the *effect* Δi on the gas pressure was next examined, on the assumption that Δi is proportional to the adsorbed chlorine, *viz.*, $\frac{x}{m}$ in the classical adsorption isotherm.

$$\frac{x}{m} = Kp^{\frac{1}{n}} \tag{2}$$

This gives

$$\log \Delta i = \frac{1}{n} \log p + \log K \tag{3}$$

The author's values of the *Joshi-Effect*, Δi, in chlorine, bromine and Cl_2–Br_2 mixture, at various applied potentials, however, showed that $\log \Delta i - \log p$ curves were not linear. This discrepancy may be attributed to the non-applicability of the isotherm to the adsorption produced under the electrical discharge. It may be also mentioned that even under normal conditions, *i.e.*, in the absence of any electrical fields in a number of cases; such as adsorption of CO_2 on charcoal[25] and water vapour by silica gel,[26] the $\log x - \log p$ curves showed marked deviations from linearity.

§7. The results in Tables I and II show a marked disparity for % Δi as recorded with the oxide-rectifier and the (serially connected) vacuo-junction; this is significant since the input current was the same. It will also be seen that especially at the low voltages, the oxide-rectifier showed a negative deflection; it changes over to the positive with an increase in the applied potential.[18,27] Precisely, similar results were observed by the author in the case of bromine vapour. This was ascribed by Joshi to its limitations as a rectifier. From his oscillographic studies[10,17] of the *effect* Δi Joshi has shown that, "the current i contains a large number of frequencies of varying strength,"[19] (in addition to the supply frequency).... "the vacuo-junction have a low capacity and negligible inductance, a stable characteristic over a wide range of applied potential V, and frequency of A.C. supply."[9] The oxide rectifier on the other hand is a more selective detector. The greater % Δi observed with it may therefore be attributed to its preferential response to some of the frequencies constituting the discharge current.

The author wishes to express his grateful thanks to Prof. S. S. Joshi, D.Sc. (London), F.R.I.C., F.A.Sc., Head of the Department of Chemistry, Benares Hindu University, for suggesting the problem, kind interest and valuable guidance.

Summary

Observations of *Joshi-Effect* Δi, were made in (*a*) air, (*b*) chlorine, (*c*) chlorine-air mixtures and (*d*) air with sorbed chlorine, under an ozoniser discharge, in the range 1–3 kilo-volts (r.m.s.), of 500 cycles frequency, using as detectors an oxide rectifier and a vacuo-junction connected in series. The *effect* was undetected with the available means in (*a*) even when mixed with traces of chlorine; it was as high as 80% current diminution in but ordinary light in (*b*) and (*c*), and remarkably enough also in (*d*). Whilst *aging* in (*b*) and (*c*) increased Δi, that in (*d*) reduced it. This decrease in (*d*), attributable to the desorption of chlorine, was markedly rapid when the system was filled with successive samples of air subjected to discharge and toplered out (but not *degassed*); finally Δi was negligibly small as in (*a*). The large Δi in (*d*) is due to sorption of chlorine under conditions of discharge and not that resulting from prolonged contact of neutral chlorine with the container walls or streaming preactivated chlorine through the ozoniser. These results confirm Joshi's theory that an adsorption-like boundary layer formed under discharge is the chief seat of Δi.

Compared with the oxide rectifier, the vacuo-junction recorded a lower Δi. Following Joshi, this is ascribed to a selective action of the former to some of the frequencies constituting the discharge current.

References

1. Joshi .. *Trans. Faraday Soc.*, 1929, **25**, 121, 139.
2. ———— .. *Curr. Sci.*, 1939, **8**, 548.
3. ———— .. *Presi. Addr., Chem. Sec., Ind. Sci. Cong.*, 1943.
4. ———— .. *B. H. U. Journal*, 1943, **8**, 99.
5. ——— and Narsimhan .. *Curr. Sci.*, 1940, **9**, 536.
6. ——— and Deshmukh .. *Nature*, 1941, **147**, 806.
7. ——— and Raghavan .. *Proc. Ind. Sci. Cong.*, 1942, Part III, pp. 62, 63.
8. Deo .. *Proc. Ind. Acad. Sci.*, 1945, **A 21**, 76.
9. Joshi .. *Ibid.*, 1945, **A 22**, 225.
10. ———— .. *Ibid.*, 1945, **A 22**, 389.
11. ———— .. *Curr. Sci.*, 1945, **14**, 35, 175.
12. ———— .. *Ibid.*, 1944, **13**, 278; 1945, **14**, 317.
13. ———— .. *Ibid.*, 1946, **15**, 281.
14. ———— .. *Proc. Ind. Sci. Cong. Phys. Sec. Abst.*, 1946, 26.
15. Cherian .. *Ibid.*, 1945, 17.
16. Shanmukharao .. *Ibid., Chem. Sec. Abst.*, 1945, 55.
17. Joshi .. *Nature*, 1944, **154**, 147.
18. Prasad .. *Proc. Ind. Acad. Sci.*, 1946, **A 24**, 514.
19. Joshi and Lad .. *Ibid.*, 1945, **A 22**, 293.
20. Joshi .. *Curr. Sci.*, 1947, **16**, 19.
21. ——— and Rao .. *Proc. Ind. Sci. Cong., Chem. Sec. Abst.*, 1942, 55.
22. Das Gupta .. *Sci. & Cult.*, 1945, **11**, 318.
23. Manley .. *Proc. Phys. Soc. (Lond.).*, 1924, **36**, 288, 291.
24. Pirani .. *Z. Physik.*, 1922, **9**, 327.
25. Burrage .. *Jour. Phys. Chem.*, 1932, **36**, 2272.
26. Allamand and Burrage .. *Proc. Roy. Soc. (Lond.).*, 1931, **A 130**, 610.
27. Goyal .. *Ind. Jour. Chem. Soc.* (communicated).

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ERRATUM

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In Equation (2), page 48,

For

$$\chi_t = \frac{1}{\gamma_t}\frac{d\gamma_t}{dt} = \frac{d(\log \gamma_t)}{dt}$$

Read

$$\chi_t = \frac{1}{\nu}\frac{d\nu}{dt} = \frac{d(\log \nu)}{dt}$$

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